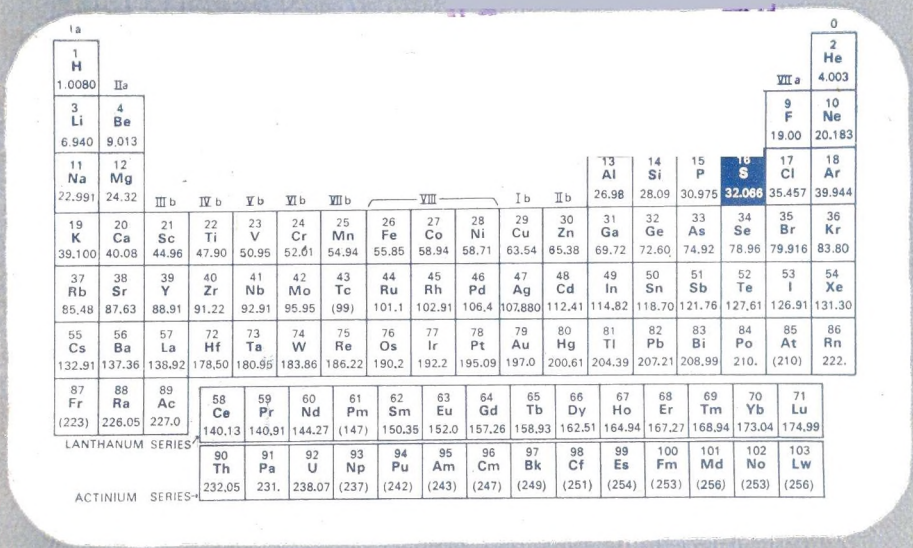
THE STORY OF THE ELEMENTS

Sulphur

(Part I)



Ia								VIII			Ib	IIb					0
1 H 1.0080	IIa															VII a	2 He 4.003
3 Li 6.940	4 Be 9.013															9 F 19.00	10 Ne 20.183
11 Na 22.991	12 Mg 24.32	IIIb	IVb	Vb	VIb	VIIb							13 Al 26.98	14 Si 28.09	15 P 30.975	16 S 32.066	17 Cl 35.457	18 Ar 39.944
19 K 39.100	20 Ca 40.08	21 Sc 44.96	22 Ti 47.90	23 V 50.95	24 Cr 52.01	25 Mn 54.94	26 Fe 55.85	27 Co 58.94	28 Ni 58.71	29 Cu 63.54	30 Zn 65.38	31 Ga 69.72	32 Ge 72.60	33 As 74.92	34 Se 78.96	35 Br 79.916	36 Kr 83.80
37 Rb 85.48	38 Sr 87.63	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.95	43 Tc (99)	44 Ru 101.1	45 Rh 102.91	46 Pd 106.4	47 Ag 107.880	48 Cd 112.41	49 In 114.82	50 Sn 118.70	51 Sb 121.76	52 Te 127.61	53 I 126.91	54 Xe 131.30
55 Cs 132.91	56 Ba 137.36	57 La 138.92	72 Hf 178.50	73 Ta 180.95	74 W 183.86	75 Re 186.22	76 Os 190.2	77 Ir 192.2	78 Pt 195.09	79 Au 197.0	80 Hg 200.61	81 Tl 204.39	82 Pb 207.21	83 Bi 208.99	84 Po 210.	85 At (210)	86 Rn 222.
87 Fr (223)	88 Ra 226.05	89 Ac 227.0															

LANTHANUM SERIES →	58 Ce 140.13	59 Pr 140.91	60 Nd 144.27	61 Pm (147)	62 Sm 150.35	63 Eu 152.0	64 Gd 157.26	65 Tb 158.93	66 Dy 162.51	67 Ho 164.94	68 Er 167.27	69 Tm 168.94	70 Yb 173.04	71 Lu 174.99
ACTINIUM SERIES →	90 Th 232.05	91 Pa 231.	92 U 238.07	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (249)	98 Cf (251)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (253)	103 Lw (256)

January–February 1978

SARABHAI M. CHEMICALS

THE STORY OF THE ELEMENTS

Sulphur

(Part One)

SARABHAI M CHEMICALS
BARODA

HISTORIC MILE-STONES

2000 (BC)	:	The EGYPTIANS used sulphur in preparing pigments and cosmetics.
1600 (BC)	:	The EGYPTIANS discovered that sulphur dioxide from the burning of sulphur had more practical value as a bleach for cotton and linen.
1000 (BC)	:	HOMER reports that Odysseus burned sulphur in his home – presumably as a fumigant – after he had slain his wife's suitors.
500 (BC)	:	The CHINESE invented Gun – powder using sulphur as an ingredient.
424 (CBC)	:	THUCYDIDES reported the application of sulphur by the tribe of BOOTIER, who in 424 BC, destroyed a city's wooden wall with a burning mass of coal, sulphur and tar.
100 or 102: BC TO 44 BC		During the time of JULIUS CAESAR, sulphur was used in the preparation of incendiary materials of warfare, in tinder boxes, and in preparing lamp-wicks for easy kindling.
50 (AD)	:	The Historian PLINY writes that sulphur possesses fourteen medical value.
MIDDLE AGES	:	The ALCHEMISTS were concerned with sulphur, because they believed that its absence, or presence in varying quantities, accounted for the difference between base metals, and the Noble metals; Silver and gold.
RENAIS-SANCE PERIOD	:	During the Renaissance period, when black powder came into universal use, sulphur became an important commodity.
15TH CENTURY (EARLY)	:	The first commercial sulphur in modern times was produced in Sicily.
15th CENTURY	:	Traveler LEO AFRICANUS once referred to sulphur-burners (*alchemists* in particular) as "stupid fellows who mummify themselves with sulphur and other horrid stinks."

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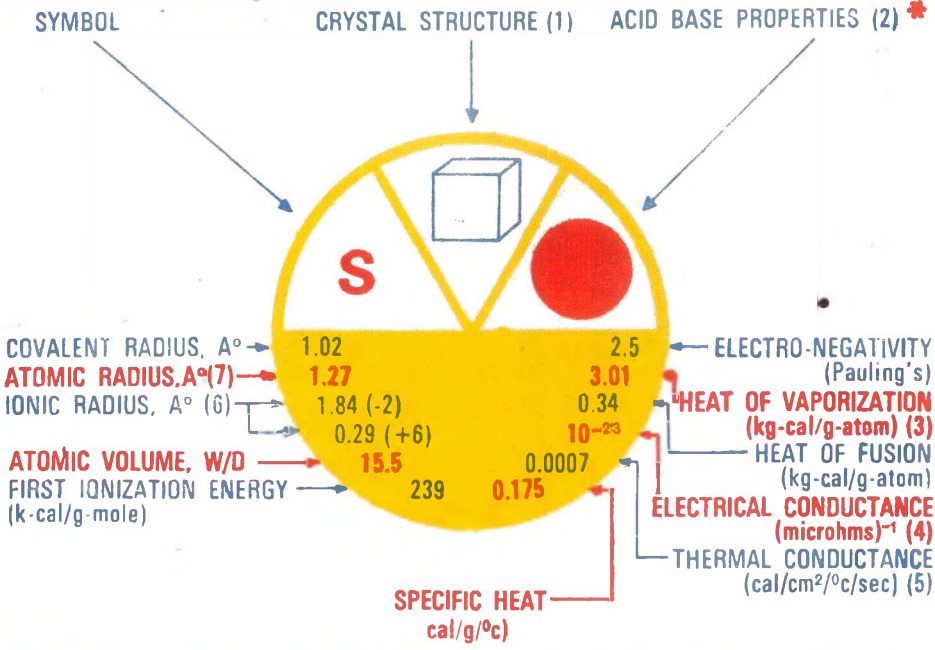
PERIODIC PROPERTIES OF SULPHUR



*

Strong

Medium

Weak

(1) Cubic

(2) Oxides of Sulphur are acidic in character, and are indicated by dark red colour. Intensity of colour indicates relative strength.

(3) At boiling point.

(4) From 0° C to 20°C.

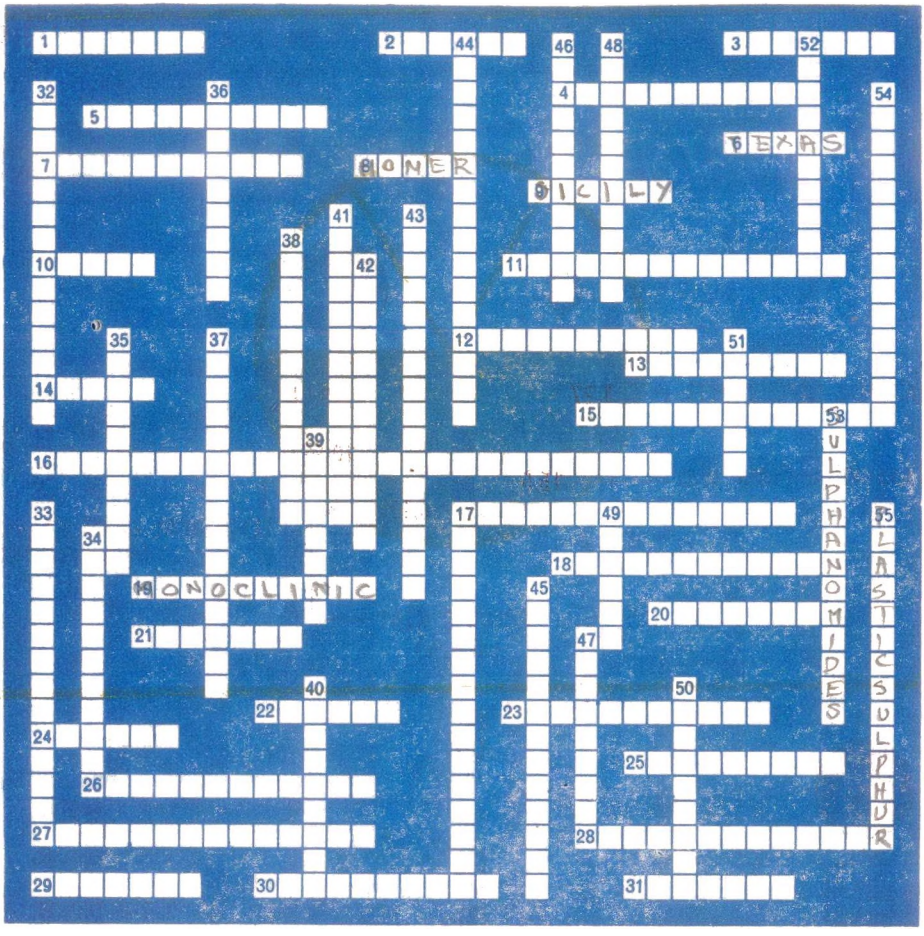
(5) At room temperature.

(6) Ionic (crystal) radii for co-ordination number 6.

(7) Metallic radii for co-ordination number of 12.

Sarabhai M Chemicals.

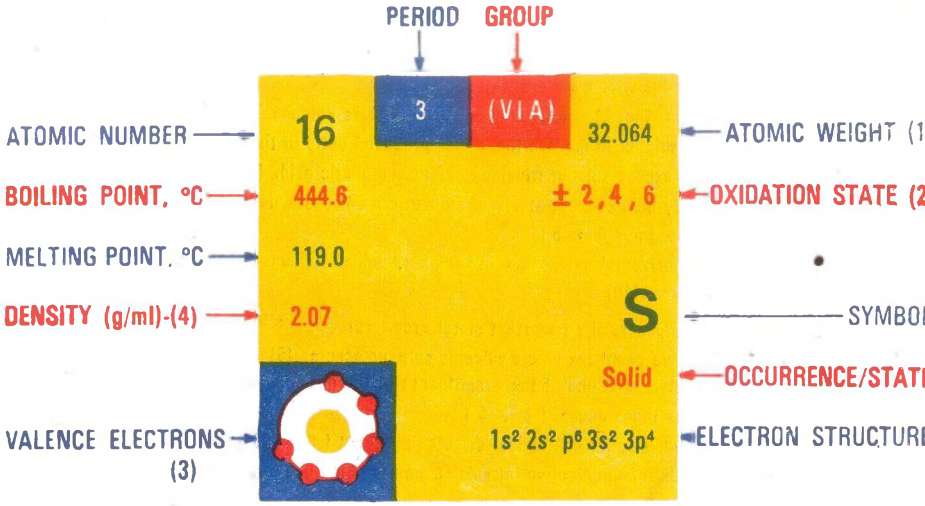
Chemistry Cross Word Puzzle (Sulphur)



HORIZONTAL LEGEND

1. The element occurring in the free state in volcanic countries known as "Brimstone" to man in the earliest period of history. Also mentioned in the Old Testament. (7)
2. The spelling of sulphur approved by the American Chemical Society and used in scientific writing in the United States. (6)
3. The most stable crystalline form of sulphur at ordinary temperatures (7)
4. When sulphur is distilled rapidly and the temperature of the receiver is above the melting point, the vapours condense as a liquid; this sulphur is collected in cylindrical container – hence a special name was derived for this variety of sulphur (4 + 7)

PHYSICAL PROPERTIES OF SULPHUR



(1) Based upon Carbon-12.

(2) The element Sulphur has three Oxidation states: ±2, 4, 6, of which ±6 is most stable.

(3) Sulphur has 6 valence electrons in its outermost orbit.

Sarabhai M Chemicals.

5. A process by which an $-OSO_2OH$ grouping is established on carbon. (10)
6. One of the two countries where volcanic sulphur is found to occur. (5)
7. The German Bacteriologist, who gave the ideas of the mechanism of action of chemotherapeutic agents, which resulted in the invention of sulpha drugs. He was the joint winner of the 1908 Nobel Prize for Medicine. (4 + 7)
8. The Greek poet to whom are attributed the epics, the Iliad and Odyssey. The Poet reports that Odysseus burned sulphur in his home – presumably as a fumigant – after he had slain his wife's suitors. (5)
9. An island in the Mediterranean – known for its Volcano "Etna" – where the first commercial sulphur in modern times was produced early in the fifteenth century. (6)
10. Solutions of excess sulphur trioxide in 100% sulphuric acid. (5)
11. Intake of very high concentrations of sulphuric acid causes death by a kind of spasm. Name this spasm. (9 + 5)
12. One of the horizontal neighbours of sulphur, which is an important ingredient of safety matches. (10)
13. A group of commercially important metal ores. (9)
14. One of the two countries where volcanic sulphur occurs. (5)
15. Hydrogen sulphide is one of the constituents in the gases ejected from a particular origin. Name these gases. (8 + 5)
16. A well known, sulphur containing, sweetening agent (6 + 20)
17. A new mode of application of sulphur paints. This use has opened the new era of application. (7 + 7)
18. A process of attaching $-SO_2OH$ grouping to nitrogen. (12)
19. An unstable form of sulphur, composed of long, needle–like crystals. (10)

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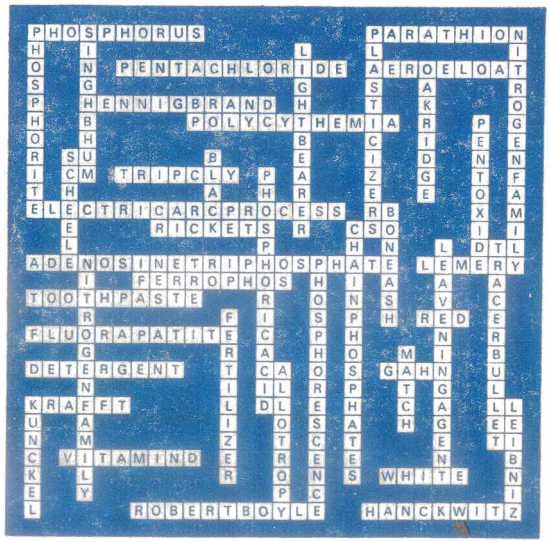


Solution to the Chemistry Cross Word Puzzle (Phosphorus) published in "The Story of the Elements" PHOSPHORUS (Part One)

SULPHUR

(PART ONE)

Sulphur, S, is a *non-metallic* element of atomic number 16 and atomic weight 32.066. Sulphur is situated in Group VIa and Period 3 of the periodic system. It is a member of *"Oxygen Family"* coming next to oxygen and to be followed by Selenium, Tellurium and Polonium, in Group VIa. Sulphur is flanked by Phosphorus and Chlorine in Period 3.

The element was discovered prior to the recorded history. Sulphur was known to the ancients and is mentioned even in the Bible, the old name *Brimstone (= 'burning stone')* remains a trade name for one type of sulphur. Sulphur is said to have known in China and India in very distant past.

Sulphur is wide-spread in lithosphere, and is one of the few elements found in nature in the elemental form. In the earth's crust it occurs as elemental sulphur; it is present in almost all minerals and ores. It is also found as an element or as its compounds in ocean, mineral springs, volcanic gases and urban atmosphere as a result of industrial activity.

Sulphur is essential to plant and animal life. Generally, hair, eggs, vegetable matters comprise of sulphur to a smaller or larger extent. Many plants contain sulphur compounds that give them distinctive flavours : for example, onion, garlic, and mustard.

Sulphur is one of the most widely used elements in industry. Either as the element or as a compound produced from the element, sulphur is basic to the manufacture of nearly everything that our present civilization produces. Sulphuric acid, most of which is produced from sulphur, is, at least so far as tonnage is concerned, the most important industrial chemical. Sulphuric acid, in turn, finds the largest field of application in the production of Fertilizers.

In the elemental form, sulphur is used in the manufacture of pulp and paper, carbon disulphide, the vulcanization of rubber, the processing of elastomers, for crop dusting, in black powder, cements, highway marking paint, in medicine, and other smaller-scale applications.

The spelling *sulfur* is approved by the American Chemical Society and is used in scientific writing in the United States; however, the older spelling *sulphur* remains current in Great Britain, Canada, India, and in other countries under *British English Language influence*, and in much commercial and popular writing in the United States.

DISCOVERY

Sulphur in its free state was well known to the ancients. In Assyrian texts (Assurbanipal, 668–626 BC) Sulphur is often mentioned as the "*product of the riverside*", which was described to have a *yellow* and sometimes *black* colour. This black colour of sulphur is certainly attributed to the presence of asphalt in it. Originally, sulphur was used for *medicinal* and *religious* purposes to purify life and ward of evils.

To the early Hebrews, sulphur symbolized *God's Wrath*, which is illustrated in various parts of the *Old Testament* (eg : destruction of Sodom and Gomorrah). The exact location of Sodom and Gomorrah is difficult to establish. The Biblical account of their destruction reads : " Then the Lord rained upon Sodom and upon Gomorrah brimstone and fire from the Lord out of heaven." (Gen. 19, 24). In his unsympathetic interpretation of Job's suffering, Bildad set forth the punishment of the wicked, and added that " *Brimstone* shall be scattered upon his habitation ". (Job, 18, 15). Ezekiel prophesied a similar upheaval which, he said, was to be accompanied by " a great shaking in the land of Israel,.....an overflowing rain, and great hailstones, fire, and *brimstone* " (Ezek. 38, 19-22).

Biblical writers used the flammability of sulphur to symbolize *torment* and destruction. In speaking of the condemned Tophet, Isaiah mentioned liquid sulphur : " the breath of the Lord, like a stream of brimstone, doth kindle it." (Isa. 30, 33). Although there seems to be no suggestion in the Bible that the Hebrews made any use of sulphur, the Greeks, even in the time of HOMER, employed it as a fumigant. In 1000 BC, Homer reports that Odysseus burned sulphur in his home – presumably as a fumigant only – after he had slain his wife's suiters. Odysseus called to Eurycleia, " Bring sulphur, old nurse, that cleanses all pollution, and bring me fire, that I may purify the house with sulphur.

PLINY described the Italian and Sicilian deposits in great detail, mentioning the use of block sulphur for medicinal purposes, the bleaching of cloth with sulphur vapour, and the manufacture of sulphur matches and lamp wicks. GEORGIUS AGIRCOLA stated that these matches could be ignited by friction on stone and used for lighting candles and dry wood. He also left no doubt as to his opinion of gun powder when he said : " Sulphur is also made to enter into that powder – execrable invention – which hurls iron, brass, or stone instruments of war of a new kind. "

It becomes a difficult task for the modern chemist to understand the early literature of sulphur, for the name was incorrectly used to designate all combustible substances. In the tenth century, Jabir believed that the metals were compounds of sulphur and mercury; and hence these two elements came to have great significance for the alchemists.

JOHANN JOACHIM BECHER,
1635 – 1682

German chemist and physician. Founder of the "Phlogiston Theory". Becher called "Terra Pinguish" to what stahl described as "Phlogiston" His experiments on minerals are described in his treatise "Physica Subterranea".
FIGURE 2

GEORGIUS AGRICOLA, 1494–1555-

German metallurgist. Author of "De Re Metallica" a famous Latin treatise on mining and metallurgy, which has been translated into English by Ex-President and Mrs. HERBERT HOOVER. Described the recovery of sulphur from its ores as well as from sulphides.
FIGURE 1

GEORG ERNST STAHL, 1660–1734

German chemist, physician and professor. Co-founder of the "Phlogiston Theory" of combustion. Author of "Fundamenta Chymial Dogmatical et Experimentalis". He distinguished between potash and soda.
FIGURE 3

ABU MANSUR mentioned the use of the former as an antidote for various kinds of metallic poisoning, and PSEUODL GEBER told how to prepare milk of sulphur by adding vinegar to alkaline sulphur solutions. Some scholars regard the Latin work : "*Invention of Verity, Or Perfection*", as a translation of an unknown Arabic treatise by Geber (Abu Musa Jabir ibn Hayyan), who lived in the tenth century A.D. It is now believed, however, that Geber (Jabir) and Pseudol-Geber (the author of the "*Invention of Verity, or Perfection*") must have been separated by five centuries of time.

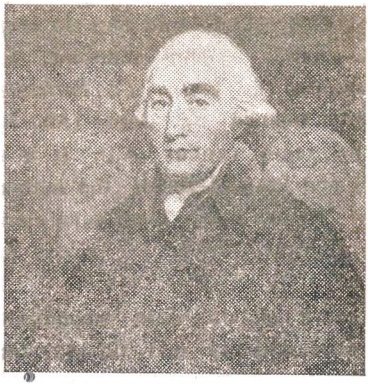
The sulphur and mercury which composed metals were recognized as being, respectively, the principles of combustibility and liquidity rather than the actual substances themselves, which were, of course, familiar to the alchemists.

The early alchemists also developed considerable practical and theoretical knowledge regarding the properties and uses of sulphur. They prepared sulphur from various minerals, and with its aid produced many new compounds and refined metals. Its particular properties also led them to develop theories which dominated chemistry for a thousand years. They regarded it as the principle of combustion (*Phlogiston*) and assumed that all combustible materials contained sulphur. This misconception delayed the recognition of sulphur as an element.

THEORY OF PHLOGISTON

The *Theory of Phlogiston*, first proposed by JOHANN JOACHIM BECHER and greatly advanced by GEORGE EARNST STAHL went back to the old idea of JABIR that combustible bodies lost *something* when they burnt. BECHER's *Terra-pinguis* became STAHL's *Phlogiston*, which was not fire itself – but the material of fire. Metals were composed of a *Calx*, different for each metal, combined with *phlogiston*, which was the same in all metals and common to all combustibles.

When a metal, such as lead or tin, was calcined in the air, *phlogiston* was evolved and a *Calx* was left behind. When a Candle or Charcoal was burnt in the air, it gave off phlogiston (manifest as heat and light) and very little residue was left; wax and charcoal mainly consisted of the material of fire. When a *calx* was heated with charcoal out of contact with air, the *phlogiston* of the charcoal recombined with the calx and the metal was regenerated.



JOSEPH BLACK, 1728 – 1799

Scottish chemist, physicist and physician. Professor of chemistry at Glasgow. He clearly characterized carbon dioxide ("fixed air") as the gas which milds the caustic alkali and distinguished between megnesia and lime. Discovered the latent heats of fusion and vaporization. Invented ice calorimenter with CAVENDISH, overthrew the "Phlogiston Theory".

FIGURE 4

HENRY CAVENDISH, 1731 – 1810

English chemist and physicist. First to distinguish hydrogen from other gases. Independent discoverer of nitrogen. Gave the first ever blow, alongwith JOSEPH BLACK, to the "Theory of Phlogiston" by their Anti-phlogistic experiments.

FIGURE 5

KARL WILHELM SCHEEL ,
1742 – 1786

Swedish pharmacist and chemist. Independent discoverer of oxygen. Discovered arsenic acid. Distinguished between nitric and nitrous acids. Discovered tungstic and molybdic acids. With JOSEPH PRIESTLEY, prepared 'dephlogisticated air' and ' phlogisticated air ' and shook the basis of the "Phlogiston Theory".

FIGURE 6

In this way, a generalisation was made which accounted for the two opposite processes of *oxidation* and *reduction*, and moreover it was able to predict certain chemical consequences which were verified later by experiments.

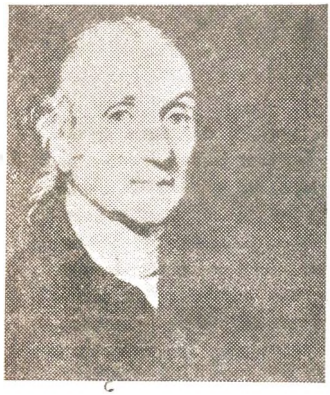
The heat given off by the animal bodies and its restoration by food were also explained by *phlogiston*. The fact that combustion and life ceased in a confined volume of air was due to the swift whirling motion of the *phlogiston* that filled the air, which when saturated could take no more. In considering the wide acceptance of STAHL's theory it must be borne in mind that it gave expression to the very striking facts that in *combustion* something was emitted by the burning body, viz., *heat*, and in the reduction of a *calx* by charcoal, something–potential energy, or the power of giving out heat again – was restored to it.

This phlogistic theory later on suffered the first blow at the hands of JOSEPH BLACK and HENRY CAVENDISH by their *Antiphlogistic Experiments*. Later on, KARL WILHELM SCHEELE and JOSEPH PRIESTLEY prepared *dephlogisticated air* and *phlogisticated air* that shook the basis of the *Phlogiston theory*. The *phlogiston theory* was virtually overthrown when ANTOINE LAURENT LAVOISIER gave the true explanation of *combustion* and *respiration*. This was the death–blow to the *phlogistic* theory.

CORTES and his daring conquisatadores made use of sulphur to prepare their *first* gunpowder. The required sulphur was obtained from the rumbling, smoking crater of Mount Popocatepetl. A brave spaniard, FRANCISCO MONTANO, descended the volcano by means of a rope, seventy or eighty fathoms, and obtained a sufficient quantity of sulphur.

Until 1849, there seems to have been no repetition of this exploit. During the 1850s, however, intrepid miners, or *volcaneros*, used to make the difficult ascent of this mountain. After being lowered by a windlass into the stifling crater, they used to collect about ten 25-pound sacks of sulphur, which they pushed over the rim of the crater and allowed to slide down the steep, snow-covered slope of the mountain. At the Tlamacas rancho the sulphur was purified by distillation.

In the year 1700, when JOSEPH–PITTON TOURNEFORT was travelling in the levant, he noticed the common occurrence of sulphur in volcanic regions near the sea. He describes : "Such are the famous volcanoes that vomit *Flames of Fire:* Vesuvius, Stromboli, Mount Aetna. Mountains



ANTOINE LAURENT LAVOISIER,
1743 – 1794

French Chemist and father of modern chemistry. Gave true explanation of combustion and respiration, and gave a death-blow to the "phlogistic doctrine" that had dominated the development of chemistry for more than a century. Was guillotined on May 8, 1794. JOSEPH LAGRANGE rightly paid homage : " It required only a moment to sever that head and perhaps a century will not be sufficient to produce another like it".

FIGURE 8

JOSEPH PRIESTLEY

English chemist. A dissenting clergyman. Celebrated discoverer of oxygen. Authored two books : "On Different kinds of Air" and "History of the corruptions of christianity" with K.W. SCHEELE, became instrumental in overtrowing the "Phlogiston Theory". He great desire was : To bless and elevate the mankind".

FIGURE 7

SIR HUMPHRY DAVY 1778 – 1829

British chemist. Isolated the alkali and alkaline earth metals and boron. Proved that chlorine is an element. Believed that sulphur was a compound containing combined oxygen.

FIGURE 9

in Iceland, Fayal, Pic-Teneriffe. In these Islands and on the Coasts of the Terra-firma of America (Panama) there are Fires which have been burning from the begining of the world..... The sulphur of Milo (= the Island of Melos) is very beautiful, and has a greenish shining Cast, which made the Ancients prefer it to that of Italy..... "

In 1759, COUNT VINCENZO MASINI of Cesena, Italy, published a patriotic poem on sulphur, in which he described its extraction, purifications and applications. In eloquent Italian verses COUNT MASINI gave poetic expression that vegetables and animals exert an influence over the formation of the metals and the so-called semi-metals :

" ..... Entro le blaze
Fra dumi, e fra dirupi il zolfo aligna,
Che piante e vegetabili pur sono
L'oro, l' argento, il rame, il ferro, il zolfo..... "

The English translation of this poem runs thus :

" .....Within the rocks, among the thorns,
Between the cliffs, sulphur takes root;
For gold, silver, copper, iron, and
sulphur Likewise are Plants..... "

The Abbe' LAZZARO SPALLANZANI described the sulphurous fumes of Volcano, and added that : " Above these fumes there is a plain, of no greater extent, which one is at first afraid to venture on, from the subterranean noise heard there, and from the shaking of the ground when struck with the foot..... On this plain it was that formerly stood the furnaces in which the sulphur of Volcano was purified. But this useful labour has long since been abandoned.....nor was it abandoned because the quantity of sulphur obtained was too little.....,as the vein is very rich and even inexhaustible. The real cause why the inhibitants of Lipari no longer continued this was that the ground ..... grows hotter and hotter the deeper it is dug into .....,to which is to be added the offensive stench of the sulphureous fumes..... "

Although sulphur has been known and used by man for thousands of years, it was considered a *strange* (rare) *earth* until LAVOISIER proved that it is an element. *Prehistoric* man used sulphur to colour his cave drawings, and supposedly ate sulphur as a *spring tonic* to purify his blood. Man discovered that the strange yellow rock would burn with an etheareal blue flame, and give off a sharp, pungent odour. This

LOUIS JOSEPH GAY LUSSAC
1778 – 1850

Professor of chemistry at the Ecole Polytechnique and at the Jardin des Plantes. Prepared potassium and isolated boron. Enunciated his famous "Law of combining volumes of gases" With THENARD, established the elementary nature of sulphur.
FIGURE 10

LOUIS JACQUES THENARD
1777 – 1857

Professor of chemistry at the Ecole Polytechnique. Discoverer of hydrogen peroxide. Collaborator with GAY LUSSAC in his researches on potassium, boron, iodine and chlorine. With GAY LUSSAC, thoroughly established the elementary nature of sulphur.
FIGURE 11

ANTOINE FRANCOIS DE FOURCROY,
1755 – 1809

French chemist of Revolutionary period. Defender of LAVOISIER's views on combustion. In collaboration with LAVOISIER, GUYTON DE MORVEAU, and BERTHOLLET, he carried out a reform of chemical nomenclature. Prepared and analyzed many reagents and medicinals. Observed an odour of hydrogen sulphide when bile was treated with hydrochloric acid or distilled.
FIGURE 12

seemingly supernatural power led him to believe that burning sulphur could be used to ward off evil spirits.

Historians report that some twenty centuries before the birth of Christ, high priests used these same qualities of sulphur to add mysticism to temple sacrifices and purification rites. These early practices were probably the origin of the notion that hellfire is fueled by brimstone. About 1600 BC, the Egyptians discovered that sulphur dioxide from burning of sulphur had more practical value as a bleach for cotton and linen. Egyptian artists, at the same time, used various sulphur compounds as colour additives for paints. Homer – the renowned Greek poet to whom are attributed the epics ; the *Iliad* and the *Odyssey* – reports in 1000 BC, that Odysseus burnt sulphur in his home after he had slain his wife's suitors.

One of the contemporary uses was developed about 500 BC, when the Chinese invented *gun-powder*, using sulphur as an ingredient. The historian PLINY writes that in AD 50, sulphur possessed fourteen medical virtues.

During the *Middle Ages*, the alchemists were concerned with sulphur, for they believed that its absence; or presence in varying quantities, accounted for the difference between base metals, and the noble metals, silver and gold. It is in these ages that sulphur was classified as one of intermediate minerals as being neither stone nor metal. Even SIR HUMPHY DAVY in 1808, believed that sulphur was a compound containing combined oxygen. It, therefore, remained for LAVOISIER to demonstrate that sulphur is an elementary substance.

During the time of the CAESARS, it was used, in tinder boxes, and in preparing lamp wicks for easy kindling. It was also used in bleaching cloth.

Very little is known regarding the production of sulphur by the ancients. Since it occurs free in nature, it was probably obtained from surface ores and containing the element in an uncombined state. During the RENAISSANCE, when black powder came into universal use, sulphur became an important commodity. Methods for its recovery were developed. AGRICOLA described its recovery not only from ores containing the free element but also from sulphides, and as early as 1530 sulphur was recovered from pyrites in Sweden. In 1740, JOSHUA WARD in England produced sulphuric acid by burning sulphur with salt petre. The

sulphuric acid industry was born, and with the birth of that industry, sulphur became of universal importance. Today, sulphur in one form or another is recognized as one of the essential elements of modern industry.

In the latter part of the eighteenth century, A. L. LAVOISIER and his adherents regarded sulphur as an element. As late as, 1809, however, SIR HUMPHRY DAVY believed that it contained oxygen and hydrogen as essential constituents and that it was similar in composition to the resins. Experiments by A. BERTHOLLET, son of C. L. BERTHOLLETS, had indicated that sulphur contains hydrogen. From his own experiments with Sicillian sulphur in 1808, SIR HUMPHRY DAVY concluded that "the existence of hydrogen is fully proved"–and that "sulphur, in its common state, is a compound of small quantites of oxygen and hydrogen with a large quantity of a basis that produces the acids of sulphur in combustion....." At last, in 1809, GAY–LUSSAC and THENARD thoroughly established the elementary nature of sulphur.

By 1810, DAVY had changed his views and suspected "a notable proportion of oxygen in sicillian sulphur, which is probably owing to the presence of oxide of sulphur.....Considering the manner in which sulphur is procured in sicily, it might be expected to contain oxygen; when taken from the mine, the limestone rock containing it, broken into small fragments, is subjected to heat in a kind of kiln, sinks, and flows out through an opening designed to give issue. This process I observed at the extensive sulphur mines in neighbourhood of Gujenti (Girgenti or Agrigentum), and I believe it is generally in use throughout the sulphur districts."

Sulphur in Louisiana and Texas

PROSPECTORS, who were boring for petroleum in Louisiana in 1865, discovered a great sulphur deposit beneath a layer of quick sand five hundred feet thick. After several companies had failed in all attempts to exploit this sulphur, DR. HERMANN FRASCH, in about 1890, began to study the problem.

The sulphur deposit, where DR. FRASCH began his work, was situated in Calcasieu Parish, Lousisiana. This deposit was buried hundreds of feet beneath successive strata of clay, gravel and quick sand which contained hydrogen sulphide. During the 1870s and 1880s, various

unsuccessful attempts were made to sink mine shafts down to the sulphur formation. This idea had finally to be abandoned after five men were asphyxiated by hydrogen sulphide. In the 1890s, DR HERMANN FRASCH, who had previously developed a process for removing sulphur from crude oil. showed his interest in the Louisiana sulphur deposit. DR FRASCH realized that the usual rock-mining processes could not be used to recover the sulphur from this Louisiana deposit economically enough to compete with Sicilian sulphur. He conceived the idea of melting the sulphur underground by injecting superheated water into the formation, and then lifting the molten sulphur to the surface with a sucker-rod pump. DR. FRASCH proceeded with his scheme and, in December 1894, pumped the first flow of molten sulphur from the Calcasieu Parish deposit. After a succession of setbacks, the *Frasch Process* was established as a commercial success, in 1902.

In recognition of his invaluable services to the mankind, he was awarded the PERKIN MEDAL, in 1912. His method of attack is carefully recorded in his acceptance of the medal :

> "To meet the extraordinary conditions existing in this deposit, I decided that the only way to mine this sulphur was to melt it in the ground and pump it to the surface in the form of a liquid . At that time, the drilling of a well in an alluvial deposit containing quick-sand, etc. was a very tedious task, and it took from six to nine months to get through the alluvial material to the rock-work, which we do today in three days.. When everything was ready to make the first trial,,.....we raised steam in the boilers, and sent the super-heated water into the ground without a hitch. If for one instant the high temperature required should drop *below* the melting point of sulphur, it would mean failure . ..
>
> "After permitting the melting fluid to go into the ground for twenty four hours, I decided that sufficient material must have been melted to produce some sulphur. The pumping engine was started on the sulphur line, and the increasing strain against the engine showed that work was being done. More and more slowly went the engine, more steam was supplied, until the man at the throttle sang out at the top of his voice : '*She's pumping*'. A liquid appeared in the polished rod, and when I wiped it off with my finger I found my finger covered with sulphur Within five minutes the receptacles under pressure were opened, and a beautiful stream of the golden fluid shot into the barrels we had already kept ready to receive the product .....When everything had been finished, the sulphur all piled up in one heap, and the men had departed ..... I mounted the sulphur pile and seated myself on the very top, It pleased me to hear the slight noise caused by the contraction of warm sulphur, which was like a *greeting from below*....."

DR. HERMANN FRASCH was educated in Germany as an apothecary's apprentice, and went to the United States at the age of sixteen years. After spending most of his life there and making many notable contributions to chemical engineering, he lived in retirement in France, where he died in 1914 at the age of sixty two years.

Sulphur in Plants

NICOLAS DEYEUX, in 1781, first demonstrated the presence of sulphur. He detected it in the roots of the dock, the cochlearia, and the horse radish. SCHEELE, however, not being sure of the discovery, thought that the plants which DEYEUX had analyzed must have grown near "hepatic air" (hydrogen sulphide) or pyrite. Sulphur is not established as an essential element for plant growth.

In many early plant analysis, only the non–volatile sulphur, which appeared as sulphates in ash, was determined. Modern analytical methods, which prevent volatilization and loss of organic sulphur compounds during the combustion, show that plants require larger amounts of sulphur than was formerly believed.

Sulphur In Animals

HEINRICH AUGUST VOGEL, in 1813, published in the "Annales de Chimie et de Physique a paper "On the existence of sulphur in the bile and in the blood". CADET and FOURCROY observed an odour of hydrogen sulphide when bile was treated with hydrochloric acid or distilled. Guided by these results, VOGEL distilled two killograms of fresh Ox bile from a large glass retort connected to a flask containing a solution of lead sulphide revealed the presence of sulphur in the bile. He also showed its presence in blood and urine. The "Encyclopedie Methodique" (1815) mentioned the presence of sulphur in albumen, hair and wool.

Commercial Production of Sulphur

The first commercial sulphur in modern times was produced in Sicily early in the fifteenth century. Competition for control of Sicilian sulphur deposits was generated in 1735 by commercial development of a process to manufacture sulphuric acid from sulphur. Sulphur production, thus, became Sicily's chief industry. A French Company, realizing the potential

value of sulphur, gained control of the Sicilian deposits in 1839 and subsequently raised the price of sulphur from $25 to $75 per ton. Other countries, particularly England and the United States, undertook the development of their own sources. They soon learned that sulphuric acid would be made from sulphur dioxide derived from the roasting of iron pyrites. As a result, Sicilian sulphur production received a severe set-back from which it never recovered.

TO BE CONTINUED

20. One of the vertical neighbours of sulphur. An amorphous red powder, which is an essential trace element in animal feeds as well as in electronics. (8)
21. A reasonably economical source of sulphur for the manufacture of sulphuric acid (6)
22. German–born American Chemist, who is best known for the process of extracting sulphur from deep underground deposits by the use of superheated steam. (6).
23. A group of compounds characterized by the presence of both sulphur and nitrogen, with high specificity for certain bacteria. (6 + 5).
24. One of the vertical neighbours of sulphur, after whom the whole "family" of Group VI A elements is known (6).
25. The scientist who first made carbon disulphide by heating pyrites with carbon (9).
26. A procedure by which the sulphonic acid group, $-SO_2OH$, or the corresponding salt, is attached to a carbon atom. (12)
27. A compound of sulphur, whose property of bleaching linen was known and practiced as early as 2000 BC in Egypt. (7 + 7)
28. A commercial variety of sulphur, which is prepared by acidifying a solution of calcium poly–sulphide. Also known as precipitated sulphur. (4 + 2 + 7).
29. The Scientist who first carried out studies on Hydrogen sulphide. Also responsible for helping in overthrowing the Phlogiston Theory (7).
30. The Scientist who first determined composition of Hydrogen sulphide. (10).
31. One of the two scientists who finally proved that sulphur was an element. (7).

VERTICAL LEGEND

32. Sulphur dioxide dissolves in water to form this weak acid (10 + 4)
33. The latest process to manufacture very concentrated sulphuric acid. In this process, SO_2 is oxidized to SO_3 by means of air only. (7 + 7)
34. The dyes which are important for the dyeing of yarn, knitted goods, and socks. (7+8).
35. A hypothetical substance or principle. During the middle ages the alchemists regarded sulphur as principle of combustibility. (10)
36. One of the two scientists who finally proved that sulphur was an element. (3 + 6)
37. A colourless, fuming liquid which finds application as a chlorinating agent in the organic synthesis (7 + 8)
38. The English meaning of the word Brimstone – by which sulphur was known to the ancients (7 + 5)
39. One of the horizontal neighbours of sulphur, which is a diatomic gas with non–combustible properties, greenish–yellow colour and pungent irritating odour. (8)
40. The scientist who first classified sulphur as an element. He also gave a death - blow to the " Theory of Phlogiston " (9).
41. A special variety of sulphur–containing cement employed in HNO_3 and HF service as well as in dyestuffs plants. (7 + 6)
42. World's first offshore sulphur mine began operations in 1960, some 7 miles off coast of Louisiana in a particular Gulf. Name this Gulf. (4 + 2 + 6)

43. A clear, faintly yellowish, highly flammable liquid with strong, disagreeable odour, which is used as a solvent for many compounds. (6 + 10).

44. A special kind of sulphur is obtained when sulphur is distilled slowly and the vapour is condensed into solid finely divided particles. Here, the temprature of the receiver is below the melting point of sulphur. (7 + 2 + 7).

17. A colourless gas, composed of Hydrogen and Sulphur, which has disagreeable and very offensive odour. Present as one of the substances expelled by volcanoes during their erruptions. (8 + 8).

45. The Lewis base : water, when added to the Lewis acid : sulphur trioxide, forms the most impartant compound of sulphur, and at the same time the most important mineral acid at all. (9 + 4).

46. About 85% of the total sulphur produced is converted to sulphuric acid, that, in turn, is used in a field which provides the basis to the food supply of the world. (11).

47. The Latin word from which the name sulphur is derived (9)

48. Mode of use of sulphur in the Rubber industry (11)

49. Colour ot the elemental sulphur. (6)

50. The old name of sulphur, known to ancients and mentioned even in the Bible, which still prevails as a trade name for one type of sulphur (9)

51. The name by which sulphur was known to Greeks. (6)

52. A group of organic compounds ressembling alcohols but having the oxygen of the hydroxyl group replaced by sulphur. (10)

53. A group of sulphur-containing chemical compound used in treating bacterial diseases. (13)

54. An obsolete process to manufacture the so-called fertilizer grade sulphuric acid. Here oxides of nitrogen are used to oxidize SO_2. (7 + 7).

55. If hot sulphur is poured in a thin stream into cold water, a brown-yellow plastic rubber-like mass is obrained. (7 + 7)

1530 : The first commercial sulphur was produced in Sicily.

1530 : Sulphur was recovered from the ore pyrites in Sweden.

1700 : JOSEPH-PITTON TOURNEFOOT, while travelling in the Levant, noticed the common occurrence of sulphur in Volcanic regions near the sea.

1740 : JOSHUA WARD in England produced sulphuric acid by burning sulphur with salt petre.

1759 : COUNT VINCENZO MASINI of Cesena, Italy, published a patriotic poem on sulphur, in which he described its extraction, purification and uses.

1777 : Sulphur was first classified as an element by ANTOINE LAVOISIER.

1777 : Hydrogen sulphide was first studied by SCHEELE.

1781 : The presence of sulphur in plants was first demonstrated by NICOLAS DEYEUX.

1796 : Carbon disulphide was first made by LAMPADIUS by heating pyrites with carbon.

1796 : BERTHOLLET first determined the composition of hydrogen sulphide.

1808 : SIR HUMPHRY DAVY believed that sulphur was a compound containing combined oxygen.

1809 : JOSEPH GAY-LUSSAC and LOUIS THENARD proved sulphur as an element.

1813 : HEINRICH AUGUST VOGEL published a paper on :
"The Existence of Sulphur in the Bile and in the Blood".

1867 : OIL PROSPECTORS drilling in Calcasieu Parish, Louisiana, found the first sulphur deposit in United States.

1890s : DR HERMANN FRASCH became interested in the Louisiana sulphur deposit, to find out the process of extracting sulphur from mines.

1894 : DR. HERMANN FRASCH pumped the first flow of molten sulphur from the Calcasieu Parish deposit.

1902 : Frasch Process was, after a succession of set-backs, established as a commercial success.

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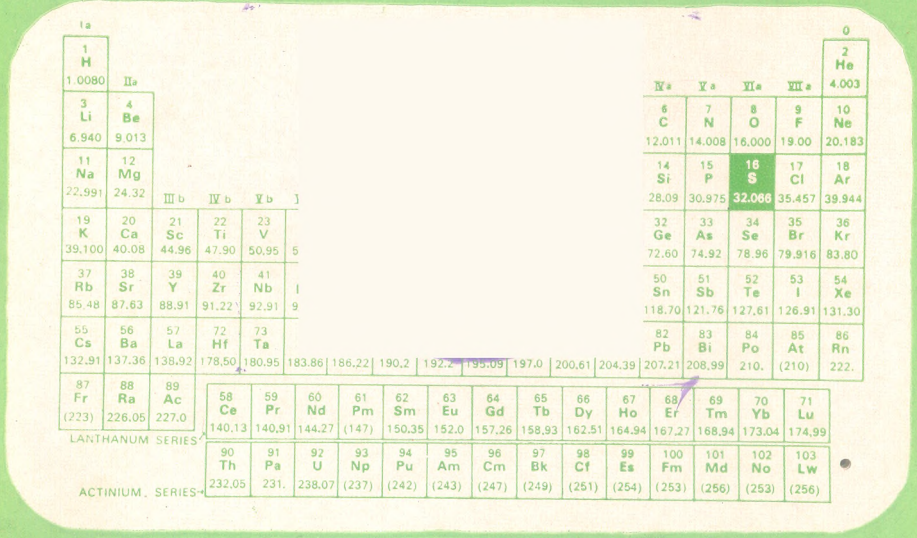
THE STORY OF THE ELEMENTS

Sulphur

(Part II)



March–April 1978

SARABHAI M. CHEMICALS

THE STORY OF THE ELEMENTS

Sulphur

(Part Two)

SARABHAI M CHEMICALS
BARODA

Woodcut showing Distillation of Sulphur in 1557

SULPHUR

(Part Two)

OCCURRENCE

SULPHUR is widely distributed over the earth. The average sulphur content of the outer crust amounts to 0.048%, which puts sulphur in 15th place in the abundance of the elements. Besides oxygen and silicon, sulphur is the most abundant element in minerals.

Sulphur occurs both in elemental form and in combination with other elements as sulphides, or sulphates. It has also been detected in stars, in cosmic clouds, and in the sun; it is estimated to be 9th in order of abundance in the cosmos. It is often found as the free element in the volcanic regions.

Significant qnantities of free and combined sulphur are found in coal and petroleum. In fact the concern for the environment has emphasized the scarcity of fossil fuels that are sufficiently low in sulphur to be burned without polluting the atmosphere. Sulphates are found in the ocean and both sulphates and hydrogen sulphide occur in many mineral waters. Although sulphur does not appear to be the natural constituent of the atmosphere, sulphur dioxide is present in most urban atmospheres as a result of industrial activity. Volcanic gases contain hydrogen sulphide.

Sulphur is essential to plant and animal life. On an average animal bodies contain about 1.6% sulphur, principally in hair and eggs; vegetable matter contains about 0.4%. Many plants contain suphur compounds that give them *distinctive flavours*, for example, onion, garlic and mustard.

Mineralogy

Many commercially important metal ores are sulphides; a few examples are listed here : *pyrite* Fe_2S ; *Chalcopyrite*, $CuFeS_2$; *Sphalerite*, ZnS ; *galena*, Pbs; *Stibnite*, Sb_2S_3 ; *Cinnabar*, HgS ; and *pentlandite*, $(Fe, Ni, Co)_9S_3$. Naturally occurring sulphates include *anhydrite*, $CaSO_4$; *gypsum*, $CaSO_4 . 2H_2O$; *kieserite*, $MgSO_4 . H_2O$; and heavy *spar*, $BaSO_4$.

Elemental Sulphur

Elemental Sulphur is pure sulphur, sometimes containing traces of arsenic, selenium, or tellurium, and often mixed with clay and/or bilumen. Sulphur is a relatively soft mineral, usually of a characteristic yellow colour, but sometimes greenish or greyish due to impurities.

Elemental sulphur chiefly occurs in sedimentary and volcanic deposits; commercial sources being; saltdomes, bedded deposits found in association with gypsum and anhydrite, extinct volcano vents, and fumaroles (hot sulphurous springs). Out of these, saltdome deposits are the largest

single source of elemental sulphur, and account for C. 60 percent of its total production in the world; these deposits occur at varying depths (upto 900 *m.*) and in various sizes.

Elemental sulphur originates by differents means. Deposits, associated with volcanism, may be formed by : condensation of sulphur vapours; reaction between H_2S and SO_2; and oxidation H_2S to H_2O and S. Sulphur may be deposited by oxidation and by sulphur bacteria from thermal springs containing H_2S. One or other of these processes has probably given rise to most of the sulphur of volcanic regions, and has also contributed to the sulphur of sedimentary beds, such as those of Silicy and Russia. Sulphur in saltdome, which is generally associated with anhydrite, gypsum, limestone, carbonaceous matter and hydrocarbons, is regarded to have originated from anhydrite through reduction by anaerobic bacterial which derive their energy from the hydrocarbons of the associated petroleum.

Distribution

Locations in the World

Sulphur is often found as the free element near active and extinct volcanic regions (impure deposits) in Japan, Sicily, Iceland, Mexico, North and South America, the Aleutians, Asia, the Italian Peninsula, New Zealand, Spain and Russia.

The largest deposits of elemental sulphur are found approximately 600 meters below ground in sedimentary deposits of anhydrite, gypsum, and calcite on top of salt domes along the coast of the Gulf of Mexico in Louisiana, Texas and Mexico. The deposits in Sicily are similar. Other noteworthy deposits occur in california. Colorado, Wyoming, Nevada, Utah, Mexico and South America.

Sulphur is also found in mineral springs. Fumarole deposits on a small scale may be seen incrusting hot springs in the Roaring Mountain or combined with the sinter deposits of the Mammoth Hot Springs in Yellowstone Park in the USA. These deposits are formed by the interaction of sulphur dioxide and hydrogen sulphide.

Solfatara, a volcanic vent emitting vapours of sulphurous character, is an another source of sulphur. The typical example is the famous solfatara, near Pozzuoli, in the Phlegraena fields west of Naples, which

has not been in active eruption since A.D. 1198, but which is continuously exhaling heated vapours, chiefly hydrogen sulphide, sulphur dioxide and steam. The term solfatara has been extended to all dormant volcanoes of this type, and a volcano which has ceased to emit lava or ashes but still evolves heated vapours is said to have passed into the "*Solfataric stage*".

At heights of 11,000–20,000 ft. in the Andes Mountains of Chile and Peru, South America, hydreds of brimstone deposits dot the area from Venezuela to Patagonia. The meagre information points to a probable reserve of hundreds of millions of tons of ore. A rich source has been uncovered in Argentina. Bolivia and Venezuela have also reported large beds of sulphur. The occurrence of brimstone has also been reported in Ecuador.

Searchers have found a number of brimstone deposits in Oceania, most of them of volcanic or hot–spring origine. The major ores occure in Java, North Celebes, White Island near New Zealand, New Hebrides, New Guinea, and the Phillipines. New Zealand possesses some deposits of volcanic origin.

A few sulphur deposits are found in Africa. They are found in Abyssinia, Egypt, Algeria and South–West Africa, Japan, Russia, China and India contain the sulphur deposits of Asia. Of these, The largest exist in Japan. The most importanr occure in northern and Central Honshu and North–eastern and South–western Hokkaido. In Iran 113 salt domes have been recognised. Not much is known about the elemental sulphur deposits of the Soviet Union.

For a long time over 50% of the World's sulphur requirements were met by pyrites. The world reserves of pyrites are widely distributed, deposits being worked in at least 30 countries. The main production in the United States occurs in the Ducktown region of Tennessee, although operations are also conducted in New York, Virginia, California, Wisconsin, Montana, Illinois Indiana and Pernnsylvania. The world's largest known reserve of pyrites is located in the southern part of Spain and Portugal. Canada, Greece, France, Germany. Russia, Italy. Japan, Finland, Sweden, and Norway also possess important deposits.

Natural sulphates occur almost every–where and this source of sulphur is practically inexhaustible. Native sulphur deposits are mined commercially in the United States, Italy, Japan and Chile.

Locations In India

Though India does not have any commercial deposits of elemental sulphur, *pyrites* – an alternative source of sulphur–is available in plenty in different parts of the country. Occurrence of sulphur and pyrites in the different states of the country are enumerated below.

ASSAM – Sulphur occurs in the form of pyrites as disseminations and nodules in some of coal varieties in the *Khasi* and *Jaintia Hills* districts. Pyrite also occurs as sparse disseminations on the northern flank of *Garo Hills*. Pyritous shales occur in large quantities with the coal–seams in *Lakhimpur* district.

BIHAR – Large and most important deposits of pyrites known in the country occur in the *Shahabad* district. Occurrences have also been recorded at *Amjhor* and *Kasisiya Koh*, and along the *Ghogha Nala*, *Barua Nala*; *Kaula Nala*, and *Jogia Nala*. Pyrite, as disseminations, occurs at several localities in *Hazaribaugh*, *Monghyr* and *Ranchi* districts. The sulphide ores of *Singhbhum* copper belt are a potential source of sulphur which can be extracted as a by–product in case it is found possible to work the deposits on large scale.

HIMACHAL PRADESH – Sulphur, as surface encrustations, occurs at *Chamba* and *Kangra* district. Pyrites is also found to occur at Rampur, Purbany, chargaon and to the North of Sungri Rest–House on the Hindustan Tibet Road.

JAMMU & KASHMIR – Deposits of amorphous crystalline sulphur, associated with gypsiferous quartz–schist, occur on the slope of Puga Valley in *Ladakh* district. This deposit is the only one of its kind in the country, but due to its difficult location, it has not assumed importance. Pyrites also occurs as disseminated grains in *Udhampur* district.

KARNATAKA – Occurrence of native sulphur has been recorded in Bellary district. Pyritic–ore has also been detected in *Chitaldrug* district. Pyrites also occurs at Guddadarangappanahalli as well as *Gulbarga*, *Kanara* and *Tumkur* districts

RAJASTHAN – An occurrence of sulphur has been reported in *Pali* district. Large deposits of pyrite/pyrrhotite are also found in the districts of *Sikar, Ajmer, Banswara,* and *Jhunjhunu.*

TAMIL NADU – An efflorescent deposit of sulphur is reported to be occurring at a swamp in the *' Wodiapollianm Jungle '* in the *South Arcot* district. Pyrite, in combination with pyrrhotite, occurs in the North Arcot district. Iroe pyrite, frequently associated with gold, is found in the region of *Nilgiri* district. *Tiruchchirapalli* district also possesses some pyrites–ore mines.

OTHER STATES – In addition to the above, occurrences of native sulphur have also been reported *East Godaveri* and *Krishna* districts of Andhra Pradesh, *Alleppey* district of Kerala, and from *Barren Island* in the South Andamans. Pyrites is also said to have occur in *Bilaspur, Chhatarpur Chhindwara, Drug, Betul* and *Surguja* districts of Madhya Pradesh; *Subansiri* district of Arunachal Pradesh; *Mayurbhanj* and *Sundargarh* districts of Orissa; *Almora, Dehra Dun, Garhwal* and *Mirzapur* districts of Uttar Pradesh; and *Jalpaiguri* district of West Bengal.

By—Product Sulphur

Sulphur has also been recovered as a by–product of mining, metallurgical and chemical operations for many years. An appreciable quantity is derived from smelters treeting sulphide ores for the recovery of metals. It is also assumed that stack gases will increase as an important source of sulphur. Growing need for fertilizer will accelerate the recovery of sulphur from smelters and power plants.

Recovery of sulphur in elemental form from hydrogen sulphide in natural gas and in refinery gases is a development of recent years. Similarly the recovery of sulphur from hydrogen sulphide in coke oven gases will probably be augmented.

The amount of sulphur in coal, as coal brasses, is very great because of enourmous reserves of coal in the world. It occurs usually as marcasite in the form of lenses, nodules and sheets in both horizontal planes and vertical fissures in coal seams. In addition, sulphur occurs in microscopic form, probably combined with organic matter. Coal brasses have been recovered and used as a source of sulphur in comparatively

small amounts Sulphur may also be recovered from coke over gases, gases from power plants burning coal, and underground gasification of coal.

Over the years to come inventions, research, and new methods could bring about profound changes and developments in the sulphur industry that cannot be visualized at present. The *Frasch process* for producing pure sulphur in one simple operation is an outstanding example of such an occurrence early in this century. Regardless of unforeseen developments, the known and potential resources of sulphur in the world will undoubtedly provide an abundance for all requirements, in any needed form, at very reasonable prices, and for an indefinitely great number of years.

PROPERTIES

Physical Properties

THE Element Sulphur, Chemical Symbol S, exhibits non-metallic properties, has an atomic number of 16 and chemical atomic weight 32,066, and belongs to the *Oxygen Family*. It occupies the position immediately below *Oxygen* and above *Selenium*, in the Group VI and Period 3 of the Periodic Table.

Pure solid sulphur has a *pale yellow* colour but its naturally occuring forms may be *Sulphur yellow, Straw yellow, Honey yellow, Yellowish brown, Greenish* or *Reddish to Yellowishgray*. Just above the melting point sulphur is a transparent yellow liquid, which with increasing temperature turns dark red and becomes black at 230°C. At the boiling point (444.6°C) vapours are generated which turn deep red at 500°C and a straw yellow at 850°C.

Sulphur is tasteless and odourless. It has no action on skin. It is insoluble water, highly soluble in carbon disulphide, moderately so in aromatic solvents and indifferently so in aliphatics.

The study of physical properties of sulphur becomes complicated by its many allotropic modifications. These allotropes differ in colour, solubility, specific gravity, crystalline form, and such other properties. The *Allotropy of sulphur* has been discussed elsewhere in this Journal, which

Reaction with Air

Sulphur combines directly, and usually energeatically, with most elements; exceptions being gold, platinum, iridium, and the inert gases. At room temperature, with oxygen or dry air, sulphur oxidizes very slowly to sulphur dioxide. When burned in the air, it forms sulphur dioxide and a little sulphur trioxide. Sulphur, in the presence of moist air, forms sulphurous as well as sulphuric acids.

Reaction with Mineral Acids

Sulphur reacts with hydrochloric acid in the presence of iron to form hydrogen sulphide. With concentrated sulphuric acid at 200°C, sulphur dioxide is formed. Dilute nitric acid upto 40% strenght has little effect. However, concentrated nitric acid, in the presence of bromine, oxidizes sulphur. This is a very strong exothermic reaction.

Reaction with Hydrogen & Carbon

Sulphur combines directly with hydrogen at 150–200°C to form hydrogen sulyhide. Molten sulphur reacts with hydrogen sulphide to form hydrogen polysulphides. At red heat, sulphur and carbon unite to result into carbon disulphide. This is a commercially important reaction.

Reaction with Alkali & Alkaline Earth Metals & Salts

At normal temperatures, sulphur unites vigorously with sodium, potassium, calcium, strontium and barium to form sulphides. In aqueous solutions of alkali carbonates and alkali and alkaline earth hydroxides, sulphur reacts to form sulphides, polysulphides, thiosulphates, and sulphites. With potassium chlorate, sulphur forms an explosive mixture.

Reaction with Transition Metals

At normal temperatures, sulphur unites readily with copper, silver and. mercury, Iron, chromium, tungsten, nickel, and cobalt react much less readily. In a finely divided state, zinc, tin, iron, and aluminum react with sulphur on heating. Sulphur forms an explosive mixture with zinc powder.

Reaction with Halogens

Various sulphides of the halogens are formed by the direct combination of sulphur with flourine, bromine and chlorine. No evident reaction

occurs with iodine; instead the elements remain as components of a complex mixture.

Reaction with Organic Compounds

Sulphur enters into reaction with numerous organic compounds. When dissolved in amines, chemical interaction between sulphur and the solvent is evidenced by the formation of coloured species ranging from deep yellow to orange and green. Many organic reactions involving sulphur are commercially significant. Sulphur is important in phases of the processes for the manufacture of lubricants, plastics, pharmaceuticals, dyes, and rubber goods.

Reaction with Materials of Construction

Sulphur is not considered to be corrosive to the usual materials of construction. Dry matter sulphur can be handled satisfactorily in mild steel or cast-iron equipment. Acid generating impurities, however, which may be introduced in handling and storage, create corrosive conditions; the exposure of sulphur to moist air causes the formation of acids that attack many metals.

Biological Properties

Sulphur ranks amogst the various elements that vegetable kingdom requires for their natural growth. Sulphur clearly plays an essential role in the *plant metabolism*. Without sulphur, the plant can not produce protein. Sulphur deficiency is overcome by providing sufficient amount of sulphur in the form of *fertilizers*. The other main sources through which sulphur is available to the plant are the soil and the atmospheric precipitation.

A number of enzymes and vitamins contain sulphur. The amino acids methionine and cystine also contain sulphur. The sulphur content of onion, garlic, and cruciferous plants is responsible for the peculiar flavour imported by these species.

Biological properties of sulphur have been discussed in detail in a separate chapter in this story of sulphur. N. P. Ancient scientists have demonstrated the presence of sulphur in the roots of the dock, the cochlearia, and the horse radish. The presence of sulphur has also been established in the bile, blood, urine, albumen, hair and wool.

ALLOTROPY

SULPHUR appears in a number of different allotropic modifications, that is, in various molecular aggregations which differ in solubility, specific gravity, crystalline form, etc. Like many other substances, sulphur also exhibits dynamic allotropy, that is, various allotropes exist together in equilibrium in definite proportions, depending on the temperature and pressure. The formulas for the molecules of various allotropes range from S_1 to S_n, where ^{n} is a very large but unidentified number ($^n > 10^6$). The particular allotropes that may be present in a given sample of sulphur depend to a larger extent upon its previous thermal history, the amount and type of foreign substances present, and the length of time that has been allowed for equillibrium to be attained.

In the solid and liquid states, the principal allotropes have been designated traditionally as $S\lambda$, $S\mu$, and $S\pi$. Of these, only $S\lambda$ is stable in the solid state. Upon solidification of molten sulphur $S\pi$ rapidly changes into $S\mu$, which in turn is converted into $S\lambda$, although at a much slower rate. The molecular structure of $S\pi$ has been determined to be that of octatomic sulphur chain. The symbol $S\mu$ designates longer, polymerized chains of elemental sulphur. $S\lambda$ is perhaps the most characteristic molecular form of sulphur, namely that of a crown-shaped octatomic sulphur ring designated in more recent literature as S_8^R. The allotropes differ in their solubility in carbon disulphide. $S\pi$ and $S\lambda$ are soluble in carbon disulphide, while $S\mu$ does not dissolve readily in this solvent.

Sulphur crystallizes in two distinct systems, the *rhombic and the monoclinic. Rhombic sulphur*, $S\alpha$, is stable at atmospheric pressures upto 95.5°C, where transition to monoclinic sulphur, $S\beta$, takes place. Monoclinic sulphur is then stable upto its natural melting point of 114.5°C. The basic molecular unit of both of these crystalline forms of sulphur is the octatomic sulphur ring, S_8^R.

The molecular constitution of *liquid sulphur* undergoes significant and reversible changes with temperature variations. These changes are evidenced by the characteristic temperature dependence of the physical properties of sulphur.

The molecular composition of *sulphur vapour* is a complex function of temperature and pressure; several molecular species are involved.

The many forms in which sulphur *occurs*, and its long history in both primitive and modern industry have led to a sometimes confusing nomenclature. The *principal names* in use are :

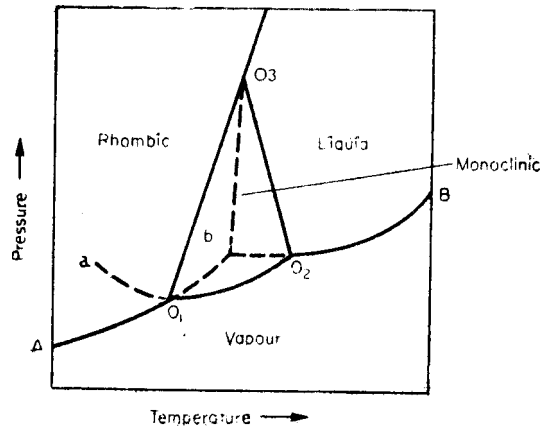


Figure 15: Phase diagram of elemental sulphur, showing the regions of temperature and pressure where rhombic and monoclinic sulphur are stable : dotted lines indicate metastable conditions.

O_1A : represents stable rhombic sulphur in equilibrium with vapour;

O_1O_2 : Stable monoclinic sulphur in equilibrium with vapour;

$aO_{I_}$: metastable monoclinic sulphur in equilibrium with vapour;

O_1 : transition temperature for change of rhombic into monoclinic sulphur;

O_2 : melting point of monoclinic sulphur in equilibrium with sulphur vapour;

O_1O_3 : effect of pressure on the transition of rhombic to monoclinic;

O_2O_3 : effect on the melting point of monoclinic.

BRIMSTONE

Sulphur was known to the ancients by *brimstone*. Mention of sulphur has been made in the Bible under the name ; *brimstone*. *Brimstone*, meaning

"burning stone" still remains a trade name for one type of sulphur. It is now defined as a *native sulphur.*

Rhombic Sulphur (Alpha Sulphur; ∝ – Sulphur)

Rhombic sulphur, also known as *alpha–sulphur* or *sulphur–α* is the commonly occuring form of sulphur. It is the stable modification of the element below 95.5°C (the transition points), and most of the other forms revert to this modification if allowed to stand below this temperature. Similarly, rhombic sulphur, depending upon the rate of heating, will get converted into *or* come into equilibrium with other varieties/ forms of sulphur. If rhombic sulphur is *heated very slowly,* it will convert into the *monoclinic* form. If the *heating rate is increased somewhat;* rhombic sulphur would ideally come into equilibrium with *liquid sulphur* only in the *lambda* form (λ–sulphur). If the *heating is rapid,* the rhombic sulphur crystallizes form a melt in which *lambda sulphur* (λ–sulphur) and *mu–sulphur* (μ–sulphur) are in equilibrium.

Rhombic sulphur lemon yellow in colour. It is *insoluble* in water; *slightly soluble* in ethyl alcohol, diethyl ether, and benzene; and *very soluble* in carbon disulphide. Its density is 2.06 g/cm^3, and its hardness is 2.5 on the Mohs scale. Its molecular formula is S_8. Its molecular configuration is a ring of eight covalently bonded sulphur atoms in the shape of a puckered crown, with bonded distances of 2.12Å ($Å = 10^{-8}$ cm) and bond angles of 105° (Figure 2).

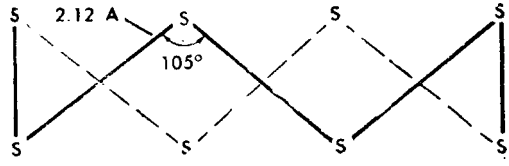


Figure 14 : The Structure of the S_8 Molecule.

Monoclinic Sulphur (Beta Sulphur; β–Sulphur)

Monoclinc sulphur, also known as *prismatic sulphur,* or *beta–sulphur* (β–Sulphur, Sβ), is the stable modification of the element *above the transition temperature* and *below the melting point.* This variety of

sulphur is obtained, in the form of needle-like, colourless prisms, when sulphur crystallizes from the molten state at a temperature near its melting point.

Monoclinic suphur has a density of 1.96 g/cm^3, and a melting point of 119.3°C. It is stable between the temperature range; 95.5 to 114.5°C. It changes to rhombic sulphur at room temperature. This form is also soluble in carbon disulphide and insoluble in water. Its molecular configuration is also an 8-atom puckered crown structure.

Nacreous Sulphur

Nacreous sulphur is a modification of ***monoclinic sulphur.*** It resembles monoclinic variety in all respects except having different axial ratios.

Lambda Sulphure (λ-Sulphur)

Lambda sulphure (λ-sulphur) is the stable solid allotrope of sulphur. It is usually encountered in commercial sulphur. Rhombic and monoclinic sulphurs are both generally considered to be of this variety.

Mu Sulphure (μ -Sulphur)

Mu Sulphur is an ordinary amorphous sulphur. It is metastable and insoluble in carbon disulphide. This variety is made by cooling very hot molten sulphur to normal temperature and then removing the soluble part by extraction with carbon disulphide; the residue is Sμ. It changes spontaneously into rhombic or monoclinic sulphur, depending upon the temperature.

PI Sulphur, (π -Sulphur)

Pi Sulphur, Sπ, is yet another form of sulphur in solid and molten sulphur. When sulphur is heated to 180°C and then cooled, it becomes more soluble in carbon disulphide. Sπ exists as a definite and distinct modification in both the liquid and solid states and is notable because of its *orange-yellow* colour. Solid π - sulphur changes rapidly into amorphous sulphur Sμ, which in turn changes into Sλ.

Plastic Sulphur (Gamma Sulphur; γ -Sulphur)

Plastic sulphur, also known as *Gamma Sulphur* (γ -Suplhur), is formed when hot sulphur is poured in a thin stream in to cold water. A *brown-yellow* plastic rubber-like mass thus obtained is known as plastic sulphur. It is an under-cooled liquid that gradually solidifies into a mixture of soluble and insoluble sulphur.

This form of sulphur is amorphous and is only partially soluble in carbon disulphide. It is thought to be composed of *two* types of sulphur : λ -sulphur ($S\lambda$, soluble in CS_2), and μ -sulphur ($S\mu$, insoluble in CS_2). These λ and μ forms probably exist in liquid sulphur also, because plastic sulphur appears to be only the super-cooled liquid. After long standing at room temperature, this form (ν) of sulphur reverts to the rhombic form.

Plastic sulphur exists as long *Zigzag Chains* of sulphur atoms, and if it is strongly stretched, it behaves like rubber because the zigzag chains are oriented in straight lines, and the material becomes fibrous and rigid.

Purple Sulphur

Purple Sulphur is formed by the sudden cooling of sulphur vapour at an elevated temperature (where the sulphur exists a S_2) to -195°C.

This purple modification is believed to be composed of S_2 units. It is unstable and readily reverts to yellow sulphur upon warming slightly to room temperature.

Flowers of Sulphur (Sublimed Sulphur)

When sulphur is distilled slowly and the temperature of the receiver is *below* the melting point of sulphur, the vapours condense into solid, finely divided particles. This type is known as flowers of sulphur or sublimed sulphur.

Roll Sulphur

When sulphur is distilled rapidly and the temperature of the receiver is *above* the melting point of sulphur, the vapours condense as a liquid.

This sulphur is often collected in *cylindrical containers,* from which the name roll sulphur was derived.

Milk of Sulphur (Precipitated Sulphur)

Milk sulphur, also known as precipitated sulphur, is a finely divided amorphous sulphur suspended in water or calcium chloride solution. Commercial sulphur is prepared by acidifying a solution of calcium polysulphide. This variety is soluble in carbon disulphide.

Colloidal Sulphur (Delta Sulphur - δ Sulphur)

Colloidal Sulphur, also called delta-sulphur (δ-sulphur), is a colloidal dispersion of sulphur in water produced by the action of gaseous hydrogen sulphide on cold, concentrated aqueous solutions of sulphur dioxide, or by decomposing sodium thio-sulphate with dilute sulphuric acid. It dissolves quite slowly in carbon disulphide.

Liquid Sulphur

Liquid sulphur exhibits the remarkable property of increasing in viscosity as its temperature is raised. Its colour becomes *dark reddish-black* as its viscosity increases and both colour darkening and viscosity reach a maximum at 200°C. Above this temperature, the colour lightens and viscosity diminishes. It is thought that at the melting point, liquid sulphur is largely Sλ (S_8 rings, yellow). and that as the temperature increases, the percentage of Sμ (polymeric sulphur chains, reddish black) also increases. At 200°C, there is thought to be a maximum of highly polymeric sulphnr chains which can interwine to give maximum light absorption and viscosity. Above this temperature, the chains break, are reduced in length, and the viscosity decreases with increasing temperature.

There is also believed to be another form of sulphur in solid as well as molten sulphur called *pi-sulphur* (Sπ), but it has not been so extensively studied as the forms already metioned and little is known about it.

A form of sulphur called *rho-sulphur* (Sp), believed to be S_6 has been reported as being obtained by the extraction of acidified aqueous sodium

thiosulphate solution with toluene. Little is known of this form of sulphur, however.

Gaseous Sulphur

Gaseous sulphur, at the normal boiling point of the element (444.60°C), is *orange-yellow* in colour. As the temperature is raised, the colour changes to deep red and then gradually becomes lighter and lighter, until it steadies at straw-yellow at 650°C.

Several molecular species are in equilibrium in gaseous sulphur : S_8,S_6.S_4 and S_2, the proportion varying with the temperature. At the normal boiling point, the vapour is largly S_8; at 750°C, it is largely S_2; and above 2000°C. it is largely dissociated into sulphur atoms

TOXICOLOGY & HAZARDS

No GENERAL statement can be made about the toxicology of elemental sulphur and its various compounds. The element itself is virtually non-toxic since comparatively large doses of sulphur may be taken internally as a medicine-without producing any mal effects or injury. However, finely divided sulphur in the form of powder or dust may be irritating, particularly to susceptible individuals.

Elemental sulphur, because of its hydrophobic character, is only slightly soluble in animal as well as human organs. Colloidal sulphur is more active than crystalline sulphur on the skin. It may cause irritation especially to the eye-lid.

Sulphur compounds, on the other hand, range from harmless to exceedingly hazardous. *Sulphur trioxide* and *sulphuric acid* are strongly irritant, and concentrated sulphuric acid is not only acidic but also a strong dehydrating agent. The care required in handling sulphuric acid is almost well known to all laboratory workers. It is extremely hazardous by indigestion also since it destroys tissues by dehydration.

Hydrogen sulphide is an extremely poisonous noxious gas, only a little less toxic than much more feared hydrogen cyanide. The odour of hydrogen sulphide is so much peculiar that it provides sufficient warning of its presence even in very low concentrations. The ability to detect the odour of hydrogen sulphide sometimes disappears with olfactory fatigue, and in higher concentrations the gas overpowers the ability of the nose to detect it. If large quantity or concentration is inhaled or ingested, respiratory paralysis and death may follow quickly unless the victim is promptly shifted to fresh air. Because of its characteristic odour, as little as 0.025 ppm is detectable, it is offensive at 3–5 ppm, strong at 20–30 ppm and less intense at 200 ppm. The maximum allowable concentration for prolonged exposure is 20 ppm. Since hydrogen sulphide is used widely in chemical laboratories, all those working with it should be made aware of its poisonous nature.

Carbon disulphide is hazardous not only as a narcotic gas but also as a highly inflammable vapour and liquid. The symptoms of chronic poisoning vary from fatigue to serious mental derangement, nervous disorders blindness, and paralysis. In higher concentrations, carbon disulphide may cause delirium, coma, and death from respiratory failure. The maximum safe permissible working concentration of carbon disulphide is 20 ppm. Carbon disulphide forms an explosive mixture with air.

Sulphur dioxide is an irritant gas. It affects the upper respiratory tract and the respiratory reflexes. It is so irritating that it is difficult to remain in a room for more than 1 minute where the concentration is 200 ppm. The acceptable permissible limit for prolonged exposure is 10 ppm.

Many sulphur halides are evil-smelling and toxic, whereas the oxyhalides have remarkable pungent and irritating odour.

Many sulphur compounds, of course, are quite innocuous : for example, the alkali and alkaline earth sulphates, some of which such as magnesium sulphate (Epsom salt) have been used medicinally.

Solid, elemental sulphur is nontoxic, however, dust-type respirators and dust tight goggles are recommended for persons who handle solid

sulphur. Because of the low ignition temperature of sulphur and its tendency to develop static charges, sulphur dust presents a fire and explosion hazard.

Liquid sulphur is a hot liquid capable of producing severe burns when it contacts skin. Liquid sulphur has a relatively low ignition point. Hydrogen sulphide gas is always present in the liquid sulphur storage tanks. Sulphur storage tanks should, therefore, have adequate roof vents to provide natural draft ventilation of hydrogen sulphide gas which may be released from liquid sulphur. All sources of ignition should be excluded from the immediate vicinity of liquid sulphur storage tanks. Personnel engaged in liquid sulphur operations should have the body completely protected by clothing, and in addition, should were safety hats. safty glasses with side shields, and heat-resistant gloves. An additional full-face shield should be worn when disconnecting piping used for transporting liquid sulphur.

First-aid treatment for skin-burns due to liquid sulphur should include the immediate cooling of the affected area with cool running water, by immersion in water, or by application of cold compresses. The sulphur crust should not be removed as it serves the purpose of sterile dressing. Further treatment should be administered by a doctor.

Excapt for the elemental sulphur and its compounds mentioned in the above discussion, each of the large number of sulphur compounds must be considered on an individual basis with regard to its toxicity or lack of it.

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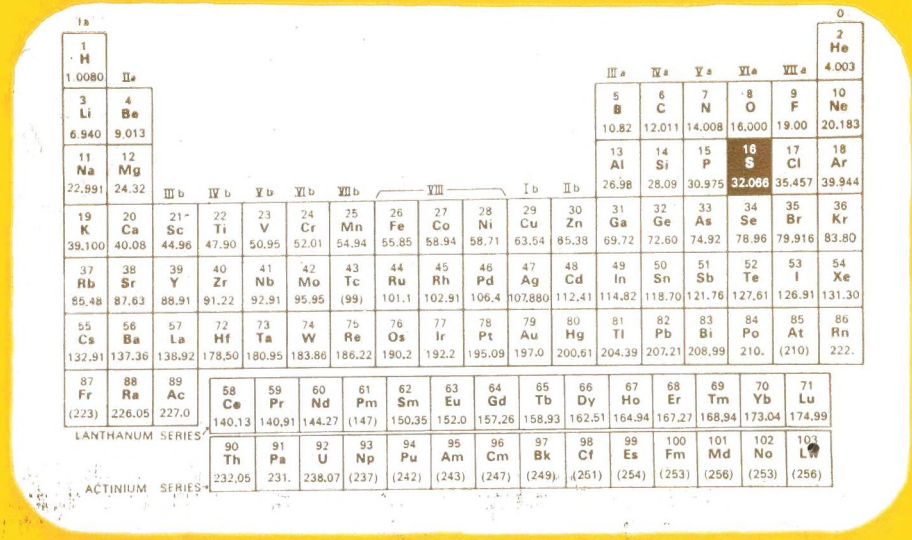
THE STORY OF THE ELEMENTS

Sulphur

(Part III)



Ia												IIIa	IVa	Va	VIa	VIIa	0
1 H 1.0080	IIa																2 He 4.003
3 Li 6.940	4 Be 9.013											5 B 10.82	6 C 12.011	7 N 14.008	8 O 16.000	9 F 19.00	10 Ne 20.183
11 Na 22.991	12 Mg 24.32	IIIb	IVb	Vb	VIb	VIIb	VIII			Ib	IIb	13 Al 26.98	14 Si 28.09	15 P 30.975	16 S 32.066	17 Cl 35.457	18 Ar 39.944
19 K 39.100	20 Ca 40.08	21 Sc 44.96	22 Ti 47.90	23 V 50.95	24 Cr 52.01	25 Mn 54.94	26 Fe 55.85	27 Co 58.94	28 Ni 58.71	29 Cu 63.54	30 Zn 65.38	31 Ga 69.72	32 Ge 72.60	33 As 74.92	34 Se 78.96	35 Br 79.916	36 Kr 83.80
37 Rb 85.48	38 Sr 87.63	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.95	43 Tc (99)	44 Ru 101.1	45 Rh 102.91	46 Pd 106.4	47 Ag 107.880	48 Cd 112.41	49 In 114.82	50 Sn 118.70	51 Sb 121.76	52 Te 127.61	53 I 126.91	54 Xe 131.30
55 Cs 132.91	56 Ba 137.36	57 La 138.92	72 Hf 178.50	73 Ta 180.95	74 W 183.86	75 Re 186.22	76 Os 190.2	77 Ir 192.2	78 Pt 195.09	79 Au 197.0	80 Hg 200.61	81 Tl 204.39	82 Pb 207.21	83 Bi 208.99	84 Po 210.	85 At (210)	86 Rn 222.
87 Fr (223)	88 Ra 226.05	89 Ac 227.0															

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ACTINIUM SERIES	90 Th 232.05	91 Pa 231.	92 U 238.07	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (249)	98 Cf (251)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (253)	103 Lw (256)

May–June 1978

SARABHAI M. CHEMICALS

THE STORY OF THE ELEMENTS

Sulphur

(Part Three)

SARABHAI M CHEMICALS
BARODA

SULPHUR

(PART THREE)

MANUFACTURE

ANCIENT PRODUCERS DESCRIBED their method of obtaining sulphur from its ores as purification by fire. Similar methods are still used in *sicily* where native sulphur ore, mined by conventional methods, is piled in open cylindrical kilns *(calcaroni)*, covered with spent ore and ignited at the top. The heat of combustion of the sulphur in the ore causes the underlying layers of suplhur to melt ; this molten sulphur is poured into molds and is then allowed to solidify. In *Japan* sulphur is usually distilled from the ore in retorts. Here, sulphur ores may be heated with steam or super heated water in autoclaves. The sulphur melts, drains from the gangue (worthless rock) and is recovered in the liquid state. Some sulphur is recovered by this method in the western

partof the *United State* also. However, after 1903, almost all U. S. sulphur was produced by the Frasch Process from the deposits located near the Gulf of Mexico in Texas and Louisiana.

Extraction of Sulphur

The extraction of sulphur is usually carried out by the several methods depending upon its occurrence. The most important one being : the Frasch Process, developed in 1891 by HERMANN FRASCH. Of lesser importance are the *Sicilian method.* (as described above) and the variation of the clause method. Sulphur can also be obtained as a by-product of many industrial processes.

Variations of the *Claus method* are sometimes used to obtain sulphur from gaseous hydrogen sulphide (H_2S), a by-product in the manufacture of many substances. It is based on the partial oxidation of the gas by oxygen in the air to give water and sulphur, according to the equation:

$$2H_2S + O_2 \xrightarrow[\text{catalyst}]{Fe_2O_3} 2\,H_2O + 2S$$

Sulphur is also obtained as a *by-product* of several industrial manufacturing processes by using coke or H_2S to reduce sulphur dioxide in flue gases.

$$SO_2 + C \longrightarrow CO_2 + S$$

$$2\,H_2S + SO_2 \longrightarrow 2\,H_2O + 3\,S$$

The *Frasch Process* is used to extract sulphur from deposits such as those in Texas and Louisiana. It consists of boring a hole from the ground surface to the sulphur-bearing calcite deposit and lowering three pipes, concentrically arranged, to the ore bed. Superheated water (165°C) is forced down the largest (6-inch) pipe into the ore bed where it melts the sulphur (m p : 112.8°C). Compressed hot air is pumped down the smallest (1-inch) pipe, and a frothy mixture of molten sulphur, water and air is forced to the surface through the intermediate (3-inch) pipe. As it comes from the well, the sulphur has a purity of 99.5-99.9% and contains virtually no arsenic, selenium or tellurium. (A separate chapter has been devoted to the FRASCH PROCESS OF SULPHUR EXTRACTION).

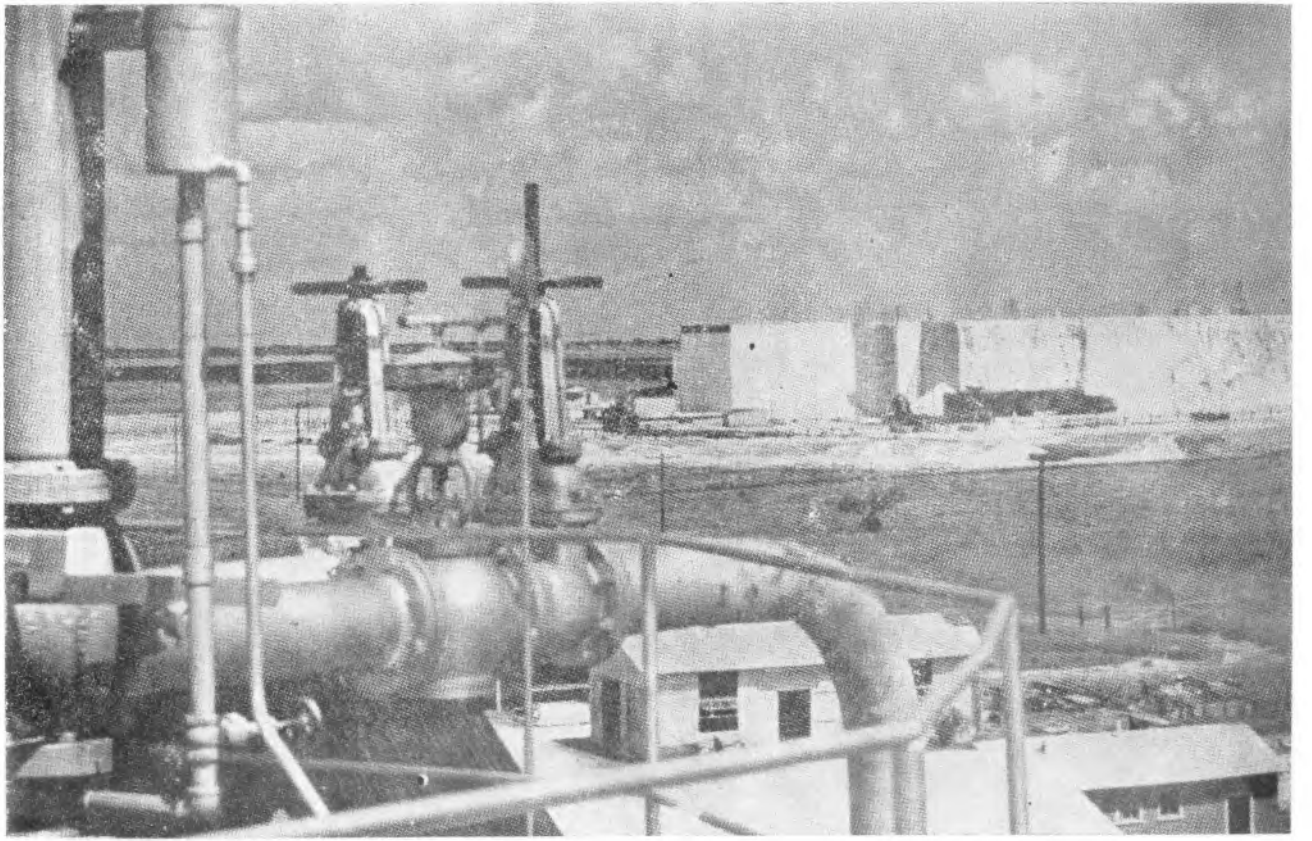


*Figure 15 : **Modern Sulphur Mining. View over Top of Processing plant. Big sulphur Vat is seen in the Background.***

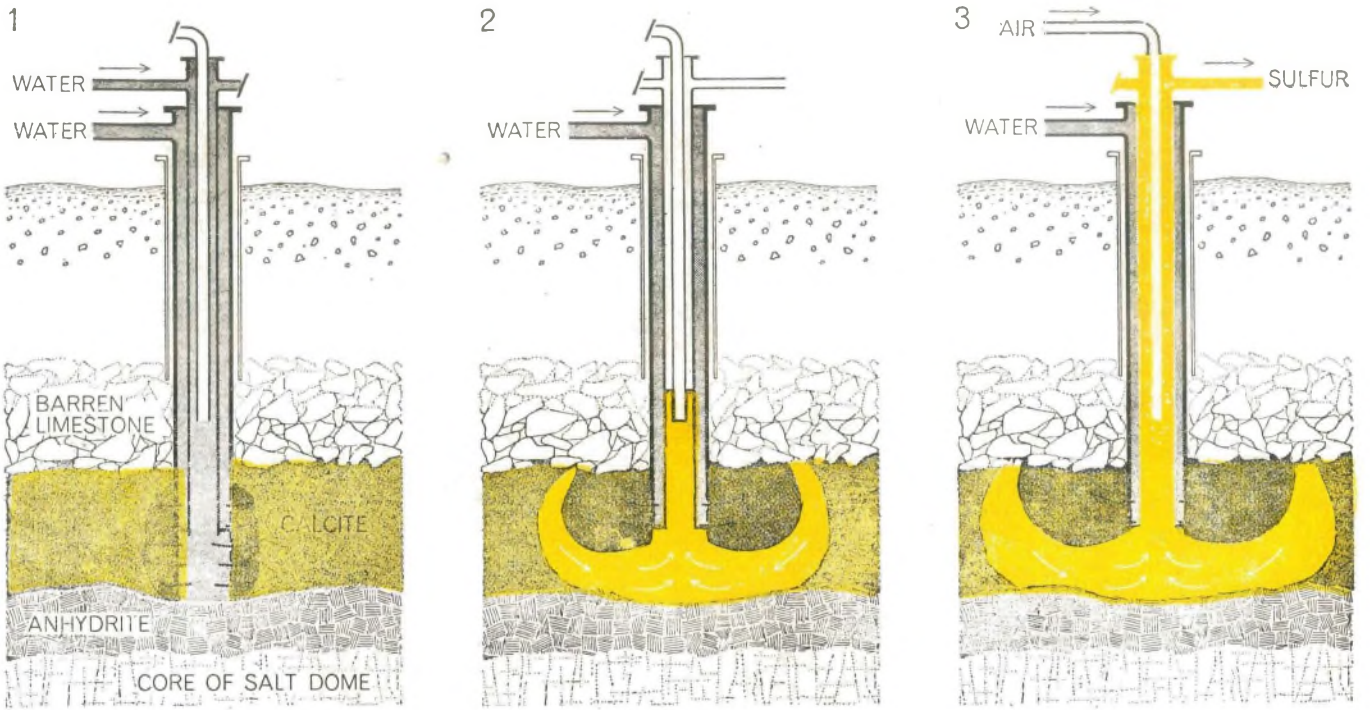
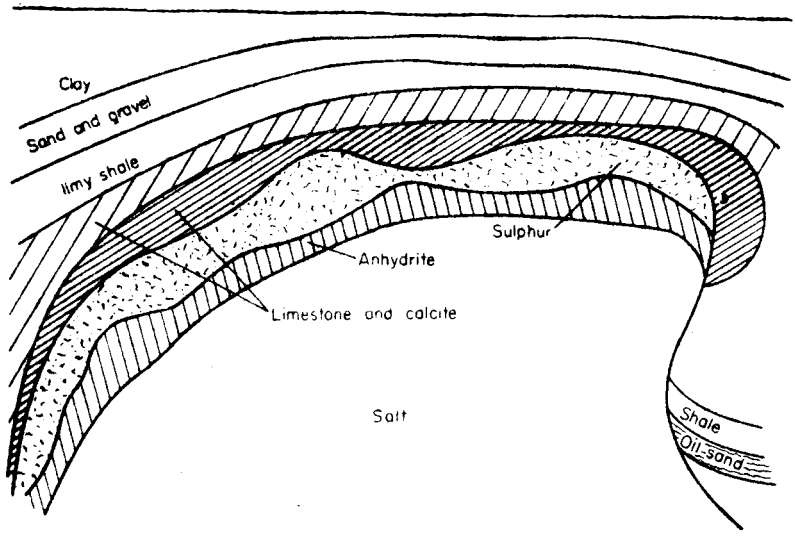


Figure 17 : FRASCH PROCESS is employed to extract sulphur from rock overlying a salt dome. The process entailes placing three concantric pipes inside a casing that lines a shaft drilled to the base of the sulphur deposit. Typical diameters for the pipes are : eight inches, four inches and one inch. Water heated to a temperature well above the boiling point is pumped (A) down the space between the four-inch pipe and the eight inch pipe, and also, in the initial stage, down the four inch pipe. It flows through the holes in the casing and into the rock where it melts the sulphur (B), which forms a pool at the bottom of the well and, under the pressure of the water, rises partway up the four-inch pipe. Compressed air forced down the one-inch pipe (C) lightens the sulphur so that it rises to the surface.

Other processes of sulphur extraction include the recovery of sulphur from *sour natural* gases, which contain high percentage of hydrogen sulphide. It is an increasingly important source of sulphur. In this process the hydrogen sulphide is stipped from the gas an ethanolamine solution and later liberated from the solvent. The hydrogen sulphide thus concentrated may be converted to sulphur by oxidation, usually by a two-step process which is summarized by the following reactions :

$$2\ H_2S + 3\ O_2 \longrightarrow 2\ SO_2 + 2\ H_2O$$

$$2\ H_2S + SO_2 \longrightarrow 3\ S + 2\ H_2O$$



Figrue : 16 Diagrammatic representation of the cap of a 'Salt dome' in Taxas.

Frasch Process for Sulphur Extraction

SEVENTY FIVE YEAR'S AGO HERMAN FRASCH perfected a new process for mining sulphur and opened up the theretofore inaccessible sources of sulphur in the Salt Domes of the Gulf of Mexico coast. His invention and the efforts of many other men led to the subsequent development of the sulphur industry, and in turn contributed to the tremendous growth of the chemical industry

In 1867, an underground sulphur deposit was discovered near Lake Charles, Louisiana, while drilling for petroleum Successively, Austrian, French and American companies attempted to reach the sulphur by modifications of conventional mining methods. All attempts ended in disastrous failures, and the rich deposit of sulphur was inaccessible

Figure 18 : View of a sulphur vat. The vat is filled with liquid sulphur and after solidification of the sulphur the walls of the vat are lifted and a further portion of liquid sulphur is poured on the top of the solidified layer. In this way enormous blocks of sulphur are formed.

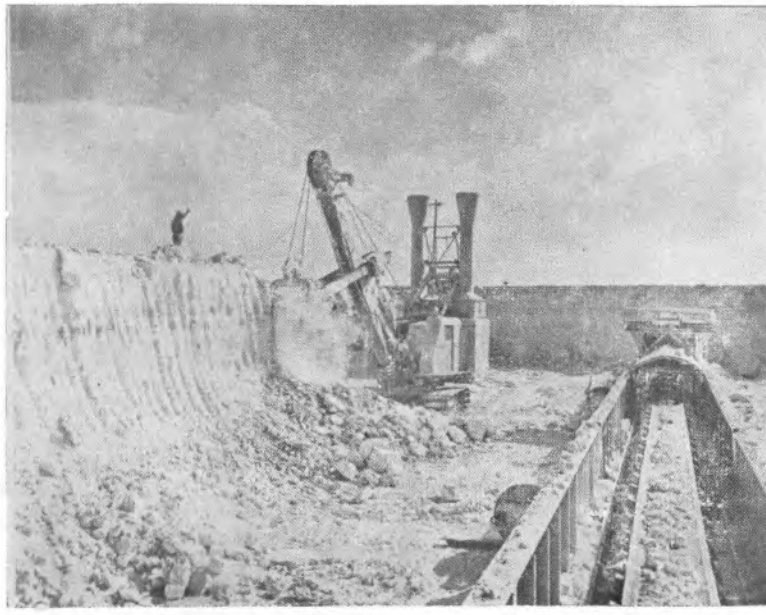


Figure 19 ; A vat of virtually pure sulphur is broken up by an electric shovel for loading into a conveyer belt at Port Sulphur, Louisiana – Freeport Sulphur Company's Storage and Shipping point on the Mississippi River.

until HERMAN FRASCH became interested. He had come from Germany at the age of 16. He worked for a few years at the Philadelphia College of Pharmacy, and at the age of 22 set up a laboratory of his own and began his career as an industrial chemist. By the time he was 36, his contributions to the technology of petroleum refining and his ownership in the Empire Oil Company in Canada had made him a wealthy man.

His interest in scientific problems, however, was in no way diminished. To mine the sulphur discovered in Louisiana he now proposed melting it under-ground with hot water, and on October 13, 1890, filed a patent application covering his idea. Many years intervened before the Union Sulphur Company which he founded in 1896 to exploit his process, achieved success. Even as late as 1901 his associates were ready to abandon the enterprise. The struggles of Frasch to make his process a success, so well described by WILLIAMS HAYNES in his book "*The Stone That Burns*", are now history. His inventiveness, ingenuity, and persevering determination which enabled him, after 16 years of difficulties and dis-appointments to convert an idea into a fabulously successful enterprise, must be admired. From his genius and his inventions the modern sulphur industry has sprung.

Frasch died in 1914. But the *pure sulphur*, which he made available through his ingenuity to the people of the world, has continued to the enourmous production of oleum products and even to some of the success in the production of the host of dyestuffs, plastics, and synthetics and many other articles now a common place feature of modern civilization.

Salt Domes

Along the gulf coast of Texas and Louisiana are numerous "Salt Domes", from which comes 95% of America's domestic elemental sulphur. These salt domes consist of a solid vertical column of *rock salt*, generally circular or elliptical in plan, extending underground from some unknown depth toward the surface, Overlying and extending upward from the top of the salt column lies a mass of rock usually consisting of *anhydrite, gypsum, calcite,* and *limestone* in the order named, and above these lie the normal sedimentary beds of *sands*, *gravels* and *clays*. There may also be found *sulphur* – usually present as crystal

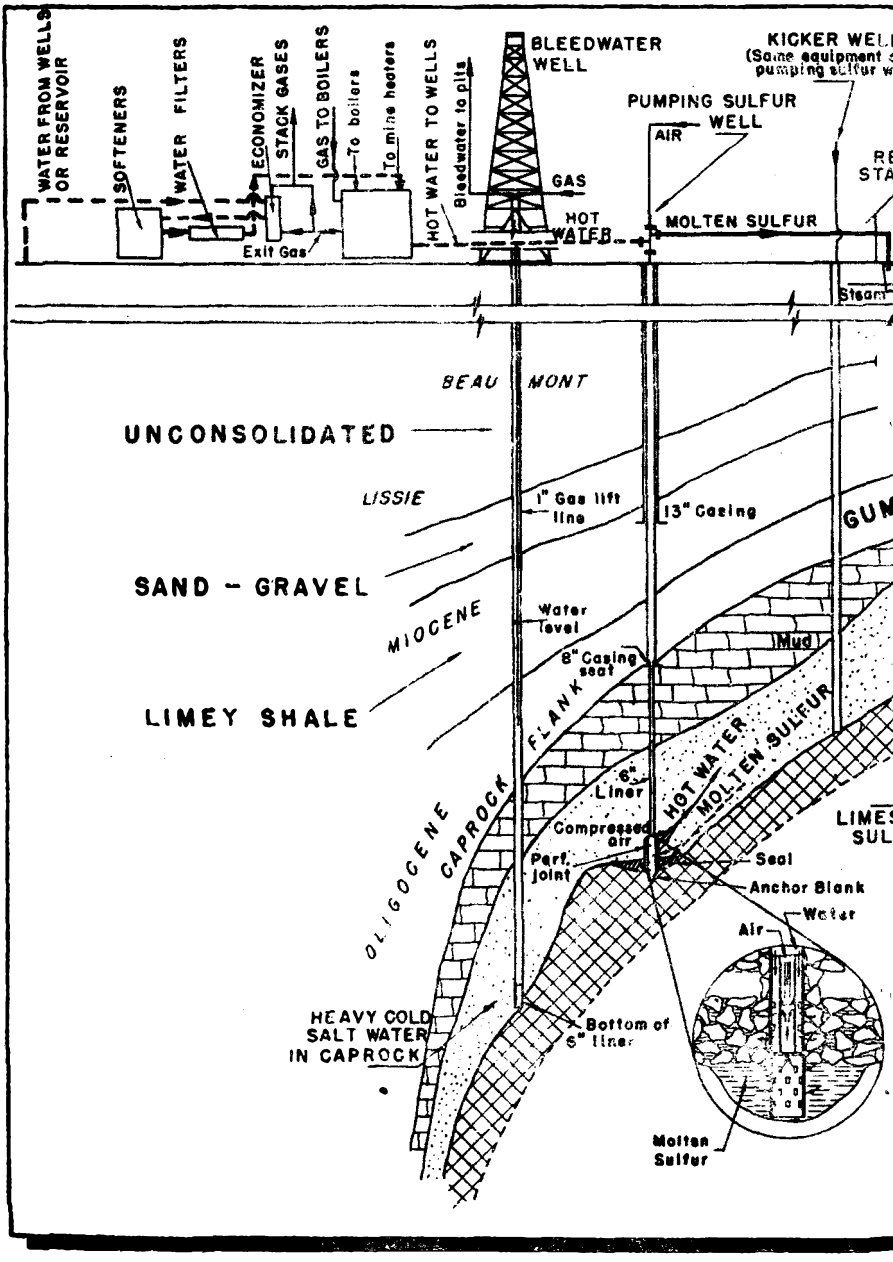
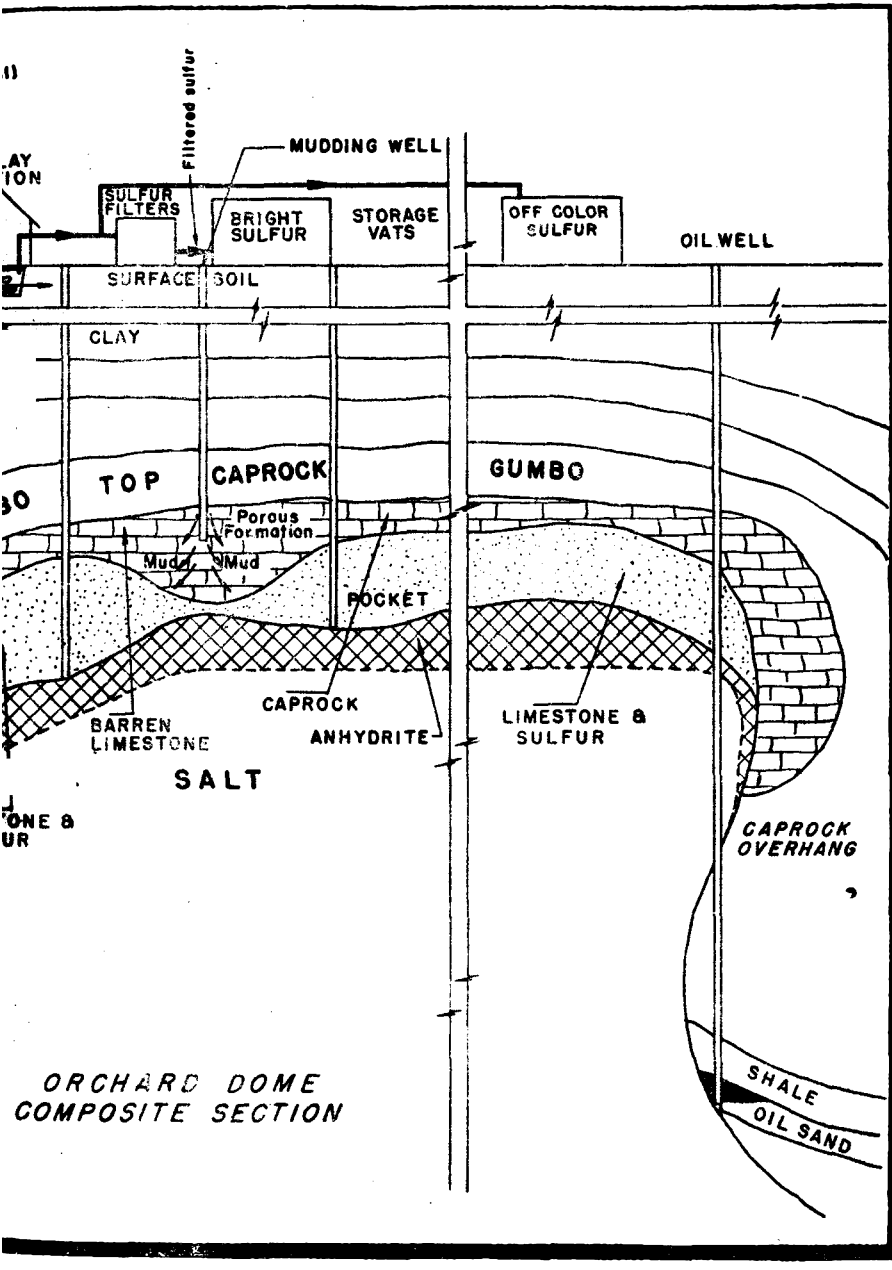


Figure 20 : Composite cross section of sulphur Dome and Elevation of Pro



ssing Plant at Mine of Duval Sulphur and Potash company, Orchard, Texas.

seams and well depositsin porous portions of the limestone or sometimes as disseminated particles in a limeston matrix in concentrations varying from mere traces to more than 50%. *(Figure 16)*.

Sulphur Wells

Once a suitable salt–dome sulphur deposit and a dependable source of fresh water are available, the mining process is accomplished in three fundamental steps :

1. Operation of a power plant which can heat large quantities of water and pump it to the site of the field operations.

2. Distribution of hot water, by means of wells, to melt the underground sulphur and elevation of the melted sulphur to the surface.

3. Cooling and solidifying the sulphur.

Since the heart of the *Frasch Process* lies in the operation of these wells, it is desirable to picture the events taking place underground which result in the fusion and collection of sulphur and its removal to the surface.

A Frasch well is installed by sinking a protective casing as far as the upper part of the anhydrite or gypsum bed underlying the sulphur-bearing stratum. Three concentric pipes are put down into the casing. First an eight inch pipe is sunk through the cap rock to the bottom of the sulphur deposit. The lower end of the pipe is perforated with small holes. Inside this pipe a four-inch pipe is lowered to within a short distance of the bottom. Last and inner most is a one-Inch pipe that reaches more than half way to the bottom of the well.

Water heated under pressure to a temperature well above its boiling point is pumped down the space between the eight–inch pipe and the four–inch pipe. The super–heated water flows through the holes of the eight-inch pipe and into the sulphur–bearing deposit. (*Figure 17A*) The sulphur melts and being heavier than water, forms a pool in the bottom of the well. The pumping of water down the four–inch pipe is then discontinued. (*Figure17B*). The static pressure of the hot water that has been forced into the rock formation then forces the liquid sulphur several

hundred feet up the four-inch pipe, (*Figure 17B*). Compressed air forced down the one-inch pipe foams and lightens the sulphur so that it rises the rest of the way to the surface (*Figure 17-C*).

At the surface, molten sulphur is either pumped to huge vats for solidification or put into steam – heated tanks for delivery later to heated ships, rail-road cars or trucks that carry it to market in molten form.

A sulphur vat, as shown in *Figure 18* is a spectacular sight. A typical vat, which is actually a huge yellow block of solidified sulphur, may be 50 feet high, 1200 feet long and 180 feet wide, and hole some 400,000 tons of sulphur.

A vat is built up by spraying molten sulphur thinly over the surface Interlocking aluminum forms around the top edge of the vat contain the sulphur until it solidifies; they are then lifted up for the next layer. The complete vat is, thus, built up slowly (*Figure 18*).

After solidification of the sulphur, when the vat is fully built to its maximum capacity, sulphur is broken out of the vat with explosive or electric shovels. The broken lumps are loaded by grabs into the waiting vehicles (*Figure 19*).

HERMAN FRASCH, in recognition of his services to the Chemical Industry, was awarded the Perkin Medal in 1912. His words have been carefully recorded in his address of acceptance of the Perkin Medal :

> "To meet the extraordinary conditions existing in this deposit, I decided that the only way to mine this sulphure was to melt it in the ground and pump it to the surface in the form of a liquid..... At that time, the drilling of a well in an alluvial deposit containing quick-sand, etc., was a very tedious task, and it took from six to nine months to get through the alluvial material to the rock-work which we do today in three days....When everything was ready to make the first trial,....we raised the steam in the boilers, and sent

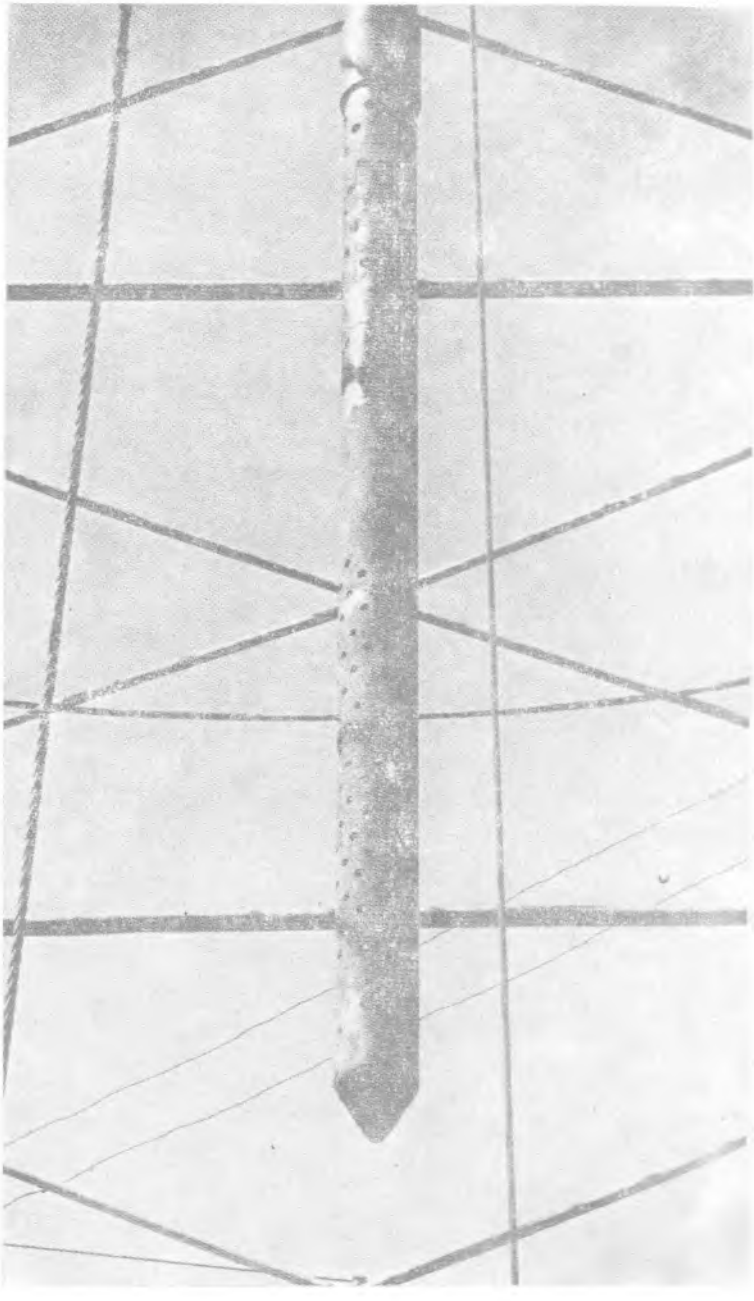
the super heated water into the ground without a hitch. If for one instant, the high temperature required should drop below the melting point of sulphur, it would mean failure....."

"After permitting the melting fluid to go into the ground for twenty-four hours, I decided that sufficient material must have been melted to produce some sulphur. The pumping engine was started on the sulphur line, and the increasing strain against the engine showed that work was being done. More and more slowly went the engine, more steam was supplied, until the man at the throttle sang out at the top of his voice, 'She's pumping'. A liquid appeared in the polished rod, and when I wiped it off with my finger I found my finger covered with sulphur. Within five minutes the receptacles under pressure were opened, and a beautiful stream of golden fluid shot into the barrels we had kept ready to receive the product....."

"When everything had been finished, the sulphur all piled up in one heap, and the men hed departed, I mounted the sulphur pile and seated myself on the very top. It pleased me to hear the slight noise caused by the contraction of the warm sulphur, which was like a greeting from below ...."

Man's adjustment to the physical world in many ways is determined by the relation between population and resources. When the methods and tools of developing the resources of a country are improved these modifications usually bring about changes in industry and in the habits and the institution of the people, and tend to raise standards of living in that country. The methods and tools for producing and using sulphur are continuously changing. New uses for sulphur and its compounds are being found. Knowledge regarding the function of sulphur in human, plant, and animal nutrition and health and disease is becoming clearer. No one knows what the coming years will bring. But it is evident from the recent advancement of science and technology that the invention of the "hot water" process of mining sulphure had a greater effect on world industry and culture.

Figure 21 : Steel pipe employed in the Frasch process is rigged for lowering into a well. When it is in place, hot water flows through the upper perforations and into the sulphur-bearing rock, and melted sulphur flows from the rock into the pipe by way of the lower perforations.



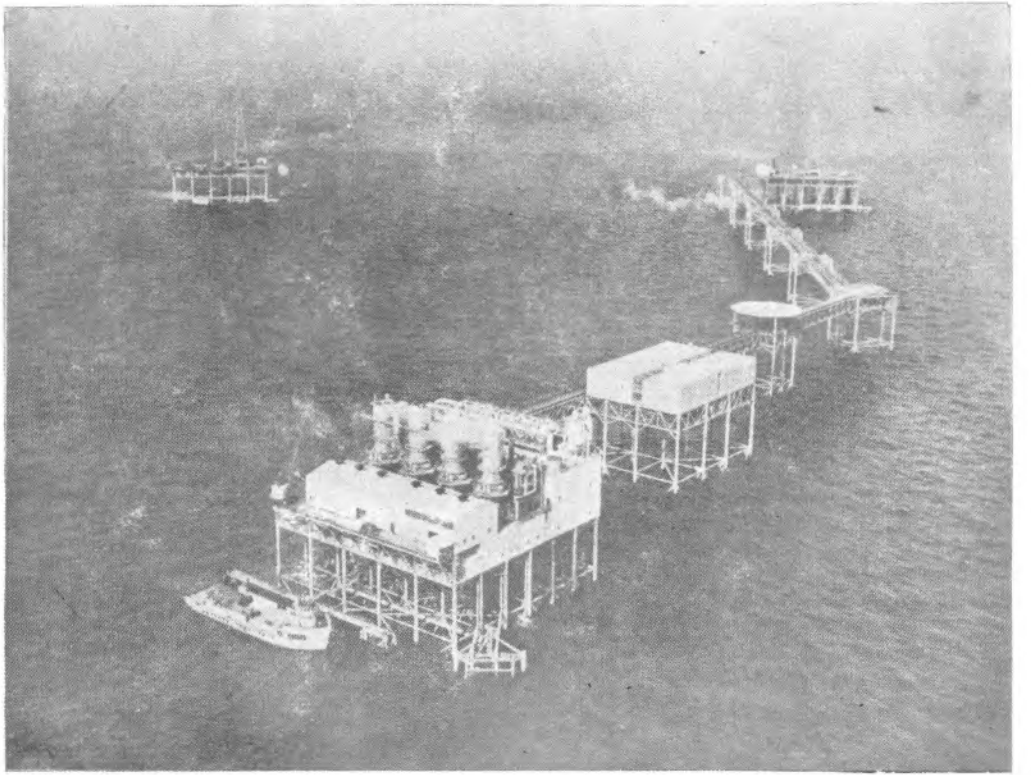


Figure : 22 World's first offshore sulphur mine, which began operation in 1960, is 7 mi off coast of Louisiana in Gulf of Maxico. In foreground is heating plant with boilers, air compressors, pumps, and generators. Other units (in order towards rear) are housing facilities, heliport and drilling and production platform.
(Courtsey : Freeport Sulphur Company, U. S. A.)

Offshore Sulphur Mining

SULPHUR MINING IN OFFSHORE operations in the *Gulf of Mexico* can be considered at the present time, only as research activities to extend known reserves. The cost off-shore construction makes sulphur mining uneccnomical on the present competitive su phur market. It is entirely feasible; in fact, overwater production of sulphur has already been accomplished in protected areas. However, the extension of this expe-rience to gulf off-shore operations, at the present time would be costly. Pipelines from offshore oil locations on the gulf floor to land-based tankage are in daily use, and the pumping of sulphur through such facilities can be accomplished.

Frasch Process

The mining of sulphur by the Frasch process in water which is shallow and reasonably protected from high wave and tide action presents no particularly difficult problem. This has been done successfully and competitively by two sulphur operating companies.

Jefferson Lake sulphur company at its Lake Piegneur operations in Louisiana, mined sulphur by using permanent wharves with drilling equipment mounted on submersible barges. When first approached, the problem of submersible barge-mounted rigs offered some interesting prospects. The case with which refloating and moving of the rigs to new locations was accomplished, was not only surprising but contributed substantially to the economy of the whole operation.

The Freeport sulphur Company, in its operations at Grande Ecaille, Louisiana, uses wharves and land-fill rig locations. They have not found the problem of overwater operation too difficult or too costly for competitive production.

The offshore prospect, of course, presents many new considerations which as yet have not been dealt with economically or competitively in sulphur production.

Of course, as long as sulphur can be produced from land-based operations and the selling price of the product is competitive, prospective operations for sulphur on the continental shelf would seem only a remote possibility. However, it does have the advantage of outlining additions to the present rapidly diminishing reserves.

The element of hurricane damage, and possible shut-down periods due to storms, must not be overlooked in any economical calculations of Frasch

process mining in gulf offshore locations. The experiences of the present offshore miners indicate that these are not insurmountable, even if they are costly.

(TO BE CONTINUED)

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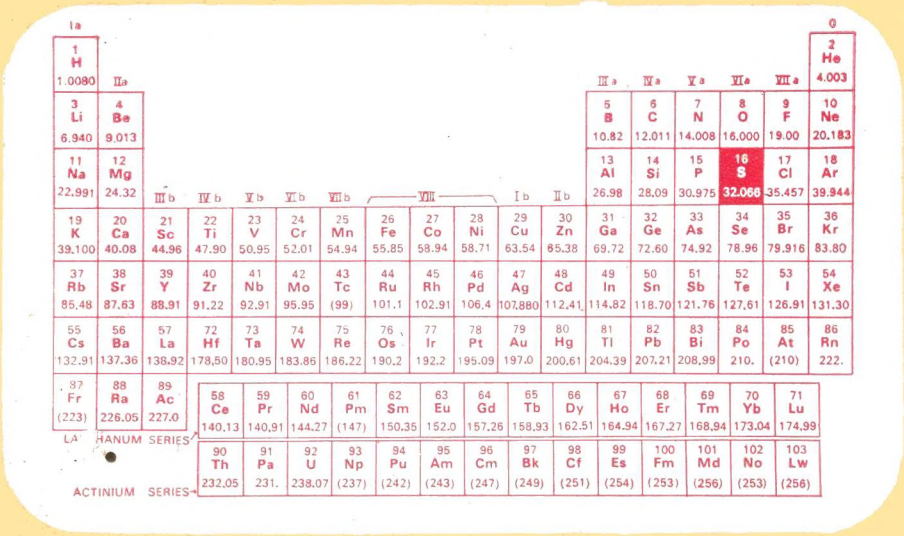
THE STORY OF THE ELEMENTS

Sulphur

(Part IV)



July-August 1978

SARABHAI M. CHEMICALS

THE STORY OF THE ELEMENTS

Sulphur

(Part Four)

SARABHAI M CHEMICALS
BARODA

SULPHUR

(Part Four)

APPLICATIONS

SULPHUR IN ONE FORM OR ANOTHER finds application in the manufacture of many products of daily use. Of all sulphur compounds, however, sulphuric acid is the most important. It is man's basic chemical and a *chemical tool* is unsurpassed.

Sulphur is used directly or indirectly in the manufacture of such a diversity of products that a nation's sulphur consumption is considered to be a barometer of its economic activity.

The largest single use of sulphur is for the production of sulphuric acid, which is then used in many other manufacturing processes. Sulphuric acid is, in turn, used primarily for the manufacture of fertilizers, organic and inorganic chemicals, pigments, steel, rayon, petroleum products, and explosives.

The principal industries using elemental sulphur as such include wood pulp, carbon disulphide, insecticide and fungicide, rubber, sugar, starch, malt and dyestuffs.

Sulphur is required for the preparation of sulphite cooking liquors in the production of sulphite pulp, and sometimes in the production of pulp by the sulphate process.

Ground crude sulphur, and flowers of sulphur, are constituents of fungicides and insecticides, and soil conditioners.

The rubber industry uses ground sulphur and specially prepared amorphous sulphur for compounding and vulconizing. Certain organic sulphur compounds act as accelerators to reduce the curing time of sulphur.

Sulphur dioxide, obtained from the combustion of sulphur, is used to decolourize beet sugar juice, and to bleach malt. The gas is absorbed in water to form sulphurous acid in the production of starch from corn and in the treatment of boiler and cooling waters.

Sulphur is used in the manufacture of certain dyes by heating organic compounds with sulphur; in the manufacture of ultramarine blue by igniting soda ash, kaolin, charcoal and sulphur; and in the manufacture of chromic oxide pigment by igniting soda sodium or potassium dichromate with sulphur.

Sulphur is also used in the manufacture of polysulphide elastomers; in making sulphur cements; in the production of free-machining steels; as a polymerization inhibitor in the manufacture of styrene monomer; and in the manufacture of matches.

Special Uses

Sulphur has been employed in various types of chemical uses for many years. Although the element possesses unusual physical properties, these have not been used to any great extent. *Building construction* and *Highway marking* are a few of the new and potential uses that utilize the unique physical properties of sulphur, sometimes requiring the addition of plasticizers or other modifiers.

Sulphur in Building Construction

The construction of concrete block walls is normally a slow process because of three factors : (1) The method of laying bricks is time-consuming. (2) When concrete blocks are used in building construction it is desirable to water-proof or decorate such structures after they have been completed. (3) A curing time is necessary before the wall achieves its maximum strength. In an improved method of wall construction the mortar is eliminated from concrete block walls by stacking the blocks one upon another and subsequently painting both sides of the wall with a special formulation, which water-proofs and decorates the wall and gives it an appreciable tensile strength.

The formulation used to paint the walls should consist of 97% sulphur, 1% plasticizers, 1%$\frac{1}{4}$-inch chopped strand glass fibers, and the remainder decorative material, such as an appropriate dye. These ingredients are heated in an open vessel to a temperature just above the melting point of sulphur and spread with a blunted brush on the surface of the concrete blocks in as thin a layer as is feasible to use. The resulting layer will be approximately 1/36 – 1/16 inch thick. The brushing operation should be carried out quickly, allowing no time for the cooling and setting of the sulphur formulation before it is properly spread. Within 5 minutes or less after spreading the formulation on the concrete block wall the material has developed its maximum strength, and the resulting wall has a substantial tensile strength. When such a wall is destroyed there is no accompanying dusting or scattering of fragments.

The new construction technique appears to be well suited for the construction of buildings designed to be waterproofed and to resist wind stress. It is particularly applicable in the areas where damage from earthquakes, tornadoes, and similar disturbances is expected. The method has the advantages of being inexpensive, rapid, and efficient. The sulphur thus applied can be subsequently painted, if desired, or left with its natural colour. Paints of conventional types adheres very well to the sulphur-coated surface.

Sulphur in High-Way Marking

Conventional types of paints, including both lacquers and plastic materials, leave a great deal to be desired in their use for marking traffic

lanes and high-ways. Some of these paints do not adhere well to asphalt. others do not wear well on concrete; many require substantial time for drying. Some plastic materials are very expensive as well as requiring appreciable time between application and use. Sulphur paints have been formulated to overcome several of these difficulties. Sulphur may be appropriately modified with polysulphide-type polymers, which stabilize and enhance its polymeric characteristics. This formulation for highway marking purposes should also contain an appropriate dye to meet the colour standards required of the paint.

The mixture of sulphur, dye and plasticizer is heated to a temperature of approximately 150°C, mixed with reflecting beads where desirable, and sprayed on the surface of the highway with a conventional type of paint sprayer modified to spray the paint at a temperature of approximately 125–130°C. Under these conditions the sulphur cools rapidly enough so that no subsequent protection is required to keep passing cars from crossing the stripe.

The fact that the plastic characteristics of the sulphur are stablized confers upon the stripe exceptionally good wearing qualities. The paint adheres very well both to asphalt and concrete surfaces without prior preparation or cleaning or priming of the surfaces. The product has been tested in wet, dry, hot and cold climates on asphalt and on concrete and has shown exceptional wear properties.

Special advantages of sulphur as a high-way marking paint are : its low cost, its exceptional wear characteristics, and its quick drying. The product can easily be made in appropriate yellow, red and black formulations, but a truly white sulphur paint has yet to be produced.

Sulphuric Acid

There is little glamour about sulphuric acid – it is not part of bomber noses, parachutes or miracle drugs. But *without* sulphuric acid neither these nor most of the catalogue of chemicals could exist. It is, indeed, the *workhorse* of the industry, and there generally is more than enough for all needs.

Sulphuric acid is important in the lives of all of us. Its consumption in a country has been said to indicate the *industrial development* of that land. Certainly no one who is familiar with industrial chemistry will gainsay the outstanding place of sulphuric acid among the materials of technology.

The production of sulphuric acid has come to be accepted throughout the world as a reliable barometer of industrial activity. Its universal use made it indispensable, in the widest sense of the word, in the chemical and process industries. There is hardly an article of commerce which has not at one time or another come into contact with sulphuric acid during its manufacture or in the manufacture of its components.

PROPERTIES

Pure (100%) sulphuric acid is a colourless liquid which is sometimes called monohydrate of sulphur trioxide because its anhydride, sulphur dioxide (SO_3) and water are combined in equimolal quantities ($SO_3 + H_2O \longrightarrow H_2SO_4$). Its specific gravity is 1.830 at 25°C (= 77°F) freezing point 10.37°C (= 50.7°F) and at one atmosphere it boils at about 340°C (= 644°F) but undergoes decomposition into sulphur trioxide and water.

The existence of the following crystalline phases has been established by the study of freezing temperatures and other properties: SO_3, $(SO_3)_2$. H_2O; i e, $H_2S_2O_7$, H_2SO_4, H_2SO_4. H_2O, H_2SO_4 $2H_2O$, H_2SO_4. $4H_2O$ H_2SO_4.6.5 H_2O and H_2SO_4. $8H_2O$.

Sulphuric acid is dibasic; that is, its molecules each contain to hydrogen atoms and ionize in two steps: $H_2SO_4 = H^+ + HSO_4^-$ and $HSO_4^- = H^+ + SO_4^=$.

Dilute sulphuric acid reacts with the more electropositive metals such as zinc, magnesium, and iron with the evoluation of hydrogen. It also reacts with metal oxides and hydroxides forming sulphates. Because of its high boiling point the concentrated acid is used to manufacture volatile acids, some of them stronger than sulphuric acid, from their salts. It liberates hydrogen chloride, (hydrochloric acid in water solution) from sodium chloride, nitric acid from nitrates, and hydrofluoric acid from calcium fluoride. It is also used to convert calcium phosphate to a more soluble acid phosphate for fertilizer and in solution displaces numerous weak acid, eg acetic and boric acids from their respective salts.

It removes by oxidation the tars and organic sulphides present in petroleum and serves as a catalyst in the sulphuric acid alkylation processes involved in the manufacture of high-octane aviation gasoline.

The concentrated acid has great avidity for water and serves as an excellent drying agent and as a dehydrating agent, removing not only moisture from gases and liquids which do not react with the acid, but extracting water from compounds. In this it chars many organic compounds such as wood, paper, cloth, starch and sugars. For the same reason the acid becomes brown in colour if it comes in contact with

traces of oil, grease or atmospheric dust. It is essential in the manufacture of explosives, celluloid, lacquers, etc., for the nitration processes involved in these processes liberate water which is removed by the sulphuric acid, thereby permitting the reactions to go to completion. Its value to *organic chemistry* is due also to its reaction with many aromatic compounds to form sulphonic acid.

Sulphates

Since sulphuric acid is dibasic, it forms both *normal* or *neutral* salts (Na_2SO_4). The latter shows acid properties in solution because of the ionization of the HSO_4^- ion and are sometimes employed for purposes requiring moderate acidity.

CHARACTERISTICS

Function

Sulphuric acid is not a *one-function* or *one-purpose* product. It is used as a drying agent, acidifying agent (pH Control), hydrolyzing agent, neutralizing, concentrating agent, dehydrating agent, oxidizing agent, polymerizing agent, purifying agent, absorbing agent, leaching agent, catalyst and active reactant in petrochemical and inorganic chemical processes.

Strength

Sulphuric acid is not a *one-strength* product. It is used in a wide range of strengths from very dilute concentrations for pH control to the strong fuming acids used in the dye, explosives, detergent, pharmaceutical and petrochemical industries. Standard market strengths are: Specific gravity 1.250 (33.33%); sp gr 1.400 (50.08%); sp gr 1.500 (59.80%); sp gr 1.835 (93.19%); 60° Baume' (77.67%); 66°Be' (93.19%); 98.00%; 20% Oleum (104.5%); 40% Oleum (109.0%); and 65% Oleum (114.63%).

These different grades have diverse markets. For instance, 53°–58° Be acid is mixed with ground phosphate rock converting it into soluble calcium phosphates, available as plant food. The 60° Be' grade is used to make the sulphates of ammonia, copper (bluestone), aluminium (alum), magnesium (epsom salts) Zinc, iron (copper as) and others; the mineral

acids; Organic acid, such as citric, oxalic, acetic and tartaric. This grade is used in pickling iron and steel before galvanizing and tinning; producing and refining heavy metals; preparing of sugar, starch and syrup; and in electroplating. The acids in the range of 93-98% are of value in purifying petroleum benzenes and oils, the preparation of titanium dioxide alkylation of isobutate; the manufacture of many nitrogen chemicals; the synthesis of pherol; and the productiod of fatty acids. The fuming grades are needed to make TNT, nitrocellulose and nitroglycerine; in dye manufacture; and to fortify the weaker acids.

Quality

Sulphuric acid is not a *one-quality* product. It is produced and supplied in exact purities for storage batteries, rayon, textile, dye, food and pharmaceutical industries; in less pure grades for steel, heavy chemical, petrochemical, fertilizer, superphosphate, and ammonium sulphate industries.

Recoverability

Sulphuric acid need not be *one-time-use* product. It can be recovered easily from some phases in the refining of petroleum and in the manufacture of explosives, petrochemicals, detergents and dyes. It is often recovered in the form unsuitable for re-use in the same process but of a strength and quality suitable for use in another process. Sulphuric acid can also be returned to the producer for fortification with sulphur trioxide or for regeneration to strong virgin acid.

Process

Sulphuric acid is not a *one-process* product. It is produced by the *Chamber Process* and the *Contact Process*.

MANUFACTURE

Early History

The date of the discovery of sulphuric acid is lost in antiquity. Perhaps the earliest reference to sulphuric acid may be attributed to IBN HAYYAN who spoke in the eighth century of distilling niter with green vitriol. ABU-BEKR-AHHASES, a Persian alhcemist who died in 940, has been

credited with its discovery. About 1250 VINCENTIUS DE BEAUVAIS mentioned it and ALBERTUS MAGNUS (1193–1280) alluded it. PARACELSUS described the process of distillation of green vitriol and the obtaining of a weak acid from the distillate. The weathering of iron pyrites usually was the source of the green vitriol.

In 1570, GERHARD DORNAEUS discussed its properties. ANDREAS LIBAVIUS told about various methods of preparation in 1595. ANGELUS SALA, in 1613, duplicated the work of Libavius. In 1666, NICOLAS LE FEVRE and NICOLAS LEMERY introduced salt peter as an improvement. CORNELIUS DREBEL improved the preparation of acid from sulphur and niter. About 1740, WARD began *"large scale"* manufacture of acid at Richmond, England, by burning sulphur in presence of saltpeter. A glass balloon flask was placed on a sand both. Eight parts of sulphur and one part saltpeter on a spoon were introduced and ignited. The vapours united with water vapour in the flask to form the acid and condensed on the side of the glass.

Chamber Process

DR. ROEBUCK of Birmingham introduced the lead chamber in 1746 and with GARBETT, built a factory at Prestonpans, Scotland, in 1749 in order to supply sulphuric acid for the bleaching of linen. A great improvement in plant operation was made in 1827 when GAY-LUSSAC introduced a tower, bearing his name, for the recovery of nitrogen oxides. In 1859, JOHN GLOVER installed the first tower, known after his name, for the denitration and concentration of the acid. The sulphuric acid chamber plant then had become complete in its essential features, and its used spread throughout the world. Various improvements and refinements have been made since then, but the basic cycle of operations, as understood and practiced by Glover and Gay-Lussac, has not been changed.

In the chamber process, sulphuric acid is prepared by burning sulphur or sulphur-bearing ores in a furnace and taking the sulphur dioxide, so formed, to large lead chambers where it reacts with oxides of nitrogen. This produces an intermediate product, nitro-sulphuric acid, which reacts with water to produce sulphuric acid and to liberate the oxide of nitrogen for re-use. The acid so produced is of low strength and quality (Figure 23).

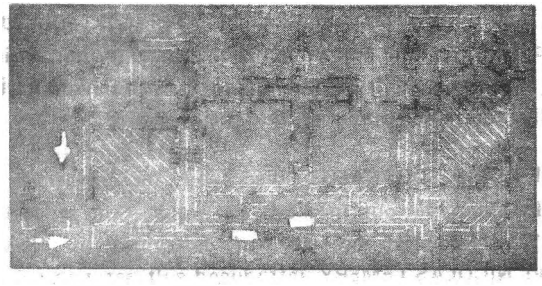


Figure 23 : The Lead Chamber Process

A–Sulphur or pyrite burners.
B–Inlet for nitrogen oxides.
C–Glover tower.
D–Lead chambers.
E–Gay – Lussac tower.
P–Pumps.

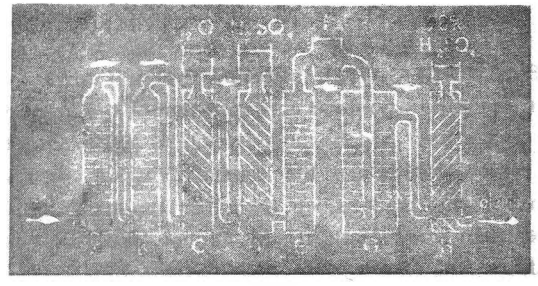


Figure 24 : The Contact Process

A–Sulphur burners.
B–Dust removal tower.
C&D–Scrubbing towers to clean sulphur dioxide.
E–Arsenic removal tower.
F–Heater.
G–Catalyst chamber.
H–Sulphur trioxide absorber tower.

Contact Process

The basic features of the present-day contact processes were described by PHILLIPS in a patent in 1831. He proposed the oxidation of sulphur dioxide over a catalyst and the absorption of the sulphur trioxide formed in water.

MAGNUS and DOBEREINER, two German Scientists, repeated his work. Magnus promoted the reaction of two volumes of sulphur dioxide and one of the oxygen to sulphuric acid with heated platinum sponge. He also formed sulphur trioxide by passing a mixture of sulphur dioxide and oxygen through a tube containing broken glass at a dull red heat. At about the same time, Dobereiner made fuming sulphuric acid with platinum black as a catalyst.

No commercial success attended the attempts to use these discoveries until EMIL JACOB, in 1875, made fuming acid from chamber acid by passing the gas from the break-down of chamber acid, over a catalyst:

$$H_2SO_4 + \text{HEAT} = H_2O + SO_2 + \tfrac{1}{2}O_2$$

The steam was condensed before the gas was led over the catalyst.

CLEMENS WINKLER advanced the fallacious conclusion that the sulphur dioxide and the oxygen should be fed to the contact mass in stoichiometric propertions and undiluted. Winkler's faulty idea held sway until 1901, when KNIETSCH disclosed the correct facts about catalytic oxidation of sulphur dioxide as a result of his work for *Badische Anilin* and *Soda Fabric* (BASF). He supplied solutions to the technical problems associated with the used of pyrites burner gas, examined the behavior of various catalysts under varying conditions showed the need for cooling of the contact mass, and generally *paved the way* for the successful operation of the *modern contact process*. BASF introduced the first ever successful contact plant into the United States in 1898.

In the contact process, sulphur dioxide is generated by burning elemental sulphur, roasting sulphur ore and/or decomposing spent sulphuric acid. The sulphur dioxide is oxidized over a catalyst to sulphur trioxide in the presence of oxygen but absence of moisture. The sulphur trioxide is then absorbed in strong sulphuric acid, combining there with water to produce more sulphuric acid, The strongest and best quality sulphuric acid is produced by this process. (Figure 24)

HANDLING

General Precautions

Sulphuric acid is classified as a corrosive liquid. Because it reacts with most metals and with water, care must be exercised in all handling operations.

In concentrations below 60° Be' (77.67%), sulphuric acid is highly reactive to metals and evolves hydrogen gas on contact. In concentrations above 77.67%, it is a strong oxidizing agent, reacting with many organic materials and inorganic reducing agents to evolve considerable heat. It is extremely avid for water and decomposes many oxygen-containing organic materials by dehydration. Addition of water to concentrated sulphuric acid will produce violent steam explosive (Spitting).

Sulphuric acid solutions, particularly the more concentrated ones, are rapidly destructive to all body tissues, causing severe burns. Repeated exposure to low concentrations may result in dermatitis. Contact with the eyes is especially hazardous, often causing severe damage and, in some cases, loss of sight.

Inhalation of the concentrated vapour from hot acid or oleum may be very harmful. Inhalation of small concentrations of the vapour over a period of time may cause chronic inflammation of the upper respiratory tract. Sensitivity to vapour is variable; 0.125 to 0,500 ppm may be mildly annoying; 1.5 to 2.5 ppm definitely unpleasant; and 10 to 20 ppm unbearable.

Although sulphuric acid is not flammable, it must be isolated from organic materials, nitrates, carbides, chlorates and metal powders. Contact of high concentrations of sulphuric acid with these materials can cause ignition. Contact of high concentrations of sulphuric acid with metallic sulphides can cause both evolution of hydrogen sulphide and ignition.

Sulphuric acid in *drums, tank cars* and *metal storage tanks* evolves hydrogen. Because 4–75% hydrogen by volume with air forms an explosive mixture, open lights or flames and spark-producing tools should be forbidden in the vicinity of such containers. All electrical fixtures in such areas must be vapour-tight.

Handling

Sulphuric is acid dangerous if improperly handled. When, however, procedural precautions are taken and adequate protective clothing is worn, there is relatively little danger in handling sulphuric acid, whatever the strength of the acid (Figure 25).

Protective Clothing

Employees who handle sulphuric acid should be provided with the following necessities : Figure 25

(a) A brimmed felt or treated-fiber hat or a rubber hat; rubber gloves; rubber high-top safety toe shoes or boots (with tops covered by trousers); woolen outer clothing fitted snugly at neck and writs; a rubber apron; a rubber acid suit for certain types of tank car loading or unloading.

(b) Water in ample quantity ready for immediately use.

(c) Suitable gas-tight chemical safety goggles.

(d) Rescue harness and lifeline for those entering a tank or enclosed storage space; an outside attendant maintaining constant observation.

(e) Proper face masks.

First Aid

Sulphuric acid causes severe burns. A doctor should be summoned immediately if the acid is swallowed or spilled, sprayed or otherwise allowed to come into direct contact with a workman's skin or eyes. In the mean time :

IN CASE OF CONTACT

Flush the skin or eyes with large quantities of water as quickly as possible and remove all contaminated clothing. Any clothing touched by acid must be removed whether penetration to the skin appears likely or not. The precaution of removal of all contaminated clothing should also be taken in minor accidents where no acid whatsoever has reached or appears likely to reach any part of a workman's body.

Figure 25 : Acid Handling – Personnel dressed in safety suit for handling sulphuric acid.

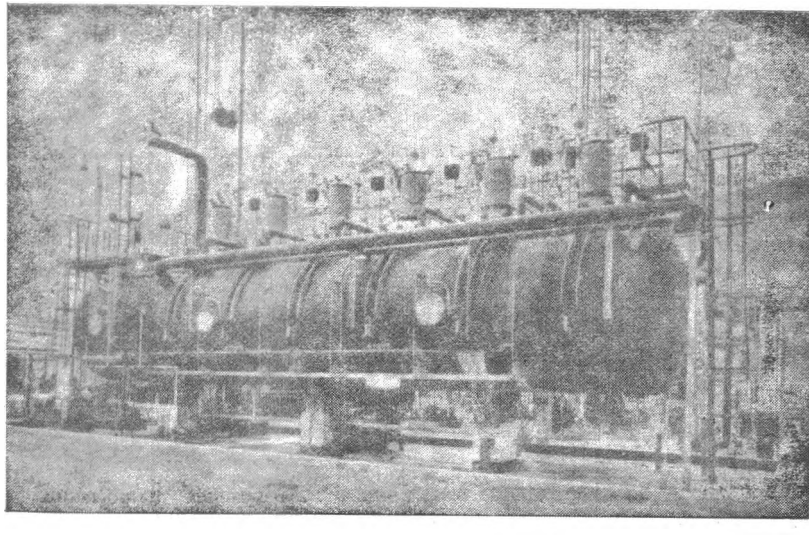


Figure 30 : Alkylation – Sulphuric acid reacts with petroleum hydrocarbons in this cascade alkylation reactor. (Courtesy : United Refining Company)

ANTIDOTE IF SWALLOWED

Drink one or more tea-spoonfuls of magnesia or chalk, or small pieces of soap softened in water with milk, mucilage or raw egg-white.

Handling Spilled Acid

Ventilate room thoroughly. Neutralize spilled acid with soda ash (sodium carbonate) or washing soda. Wash material down the drain with plenty of water. A minimum of 200 pounds of soda ash is necessary to neutralize 13 gallons of 66° Be' C (95-97%) sulphuric acid.

Transportation

Millions of tons of sulphuric acid a year are transported to various parts of the world primarily by tank car, tank truck or barge.

Large sulphuric acid consumers near a producer's plant can sometimes use pipe-lines more economically than any other means of conveyance. On the other hand, consumers of very small amount of sulphuric acid may receive the acid by common carrier but in carboys or drums rather than tank cars or tank trucks. Each container, including tank cars, must carry the identifying labes/stencils as well as the warning labels/ placards.

APPLICATIONS

Sulphuric acid is widely used in industry because of its important chemical and physical properties. Relatively low cost of sulphuric acid, incomparison to other acids having similar properties, makes it the most economical choice for a wide variety of Chemical Operations. These operations can be conveniently classified by the particular property of sulphuric acid involved.

High Boiling point

Sulphuric acid is an active acid with a high boiling point. The manufacture of halogen acids (eg : HCl;HF) and the pickling of steel make use of this high boiling point. Leaching ores, in the manufacture of metal pigments, is more effective with sulphuric acid because high leaching temperatures can be used without loss of acid by volatilization.

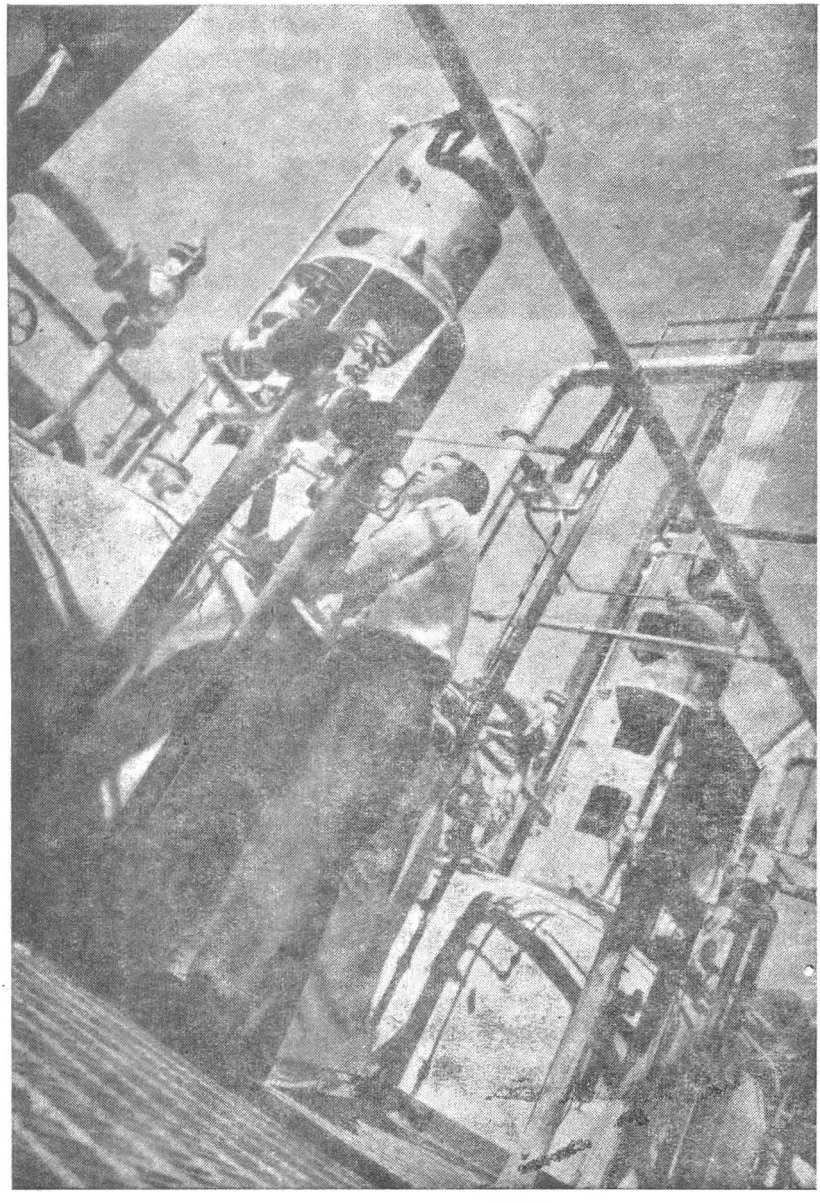


Figure 26 : Synthetic Rubber Polymerization – Sulphuric acid serves as a catalyst in the polymerization of GR-S synthetic rubber in these reactors.
(Courtesy : United States Rubber Company)

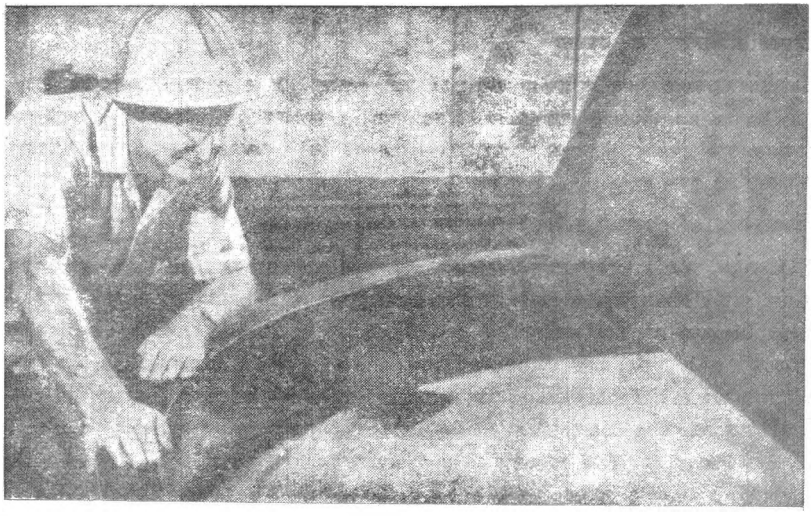


Figure 27 : Synthetic Rubber Coagulation – Sulphuric acid coagulates a high purity synthetic rubber in this steel vat.
(Courtesy : Goodyear Tire and Rubber Company)

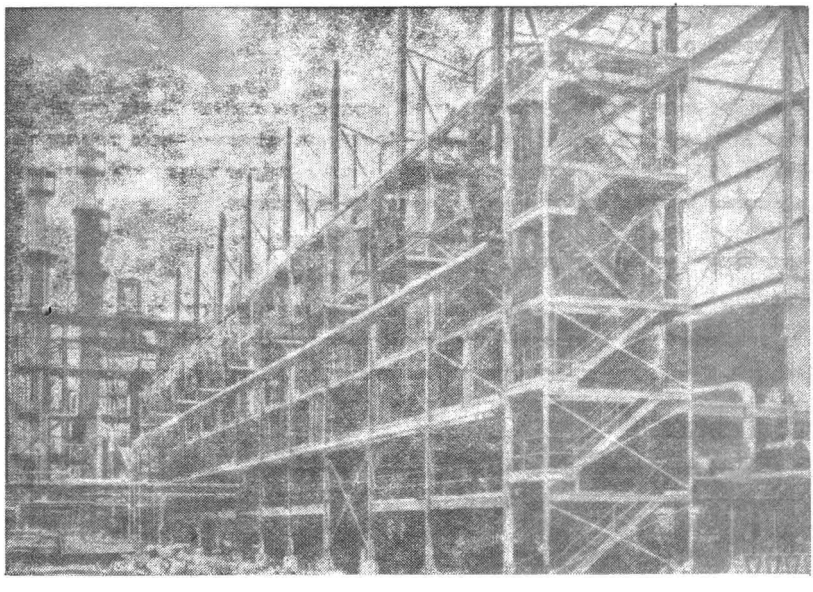


Figure 28 : Acrylonitrile synthesis – HCN and acetylene enter these tanks to begin the manufacture of acrylonitrile
(Courtesy : American Cyanamid Company)

Great affinity for water

Sulphuric acid has a great affinity for water. It is widely used for drying gases containing moisture (eg: cell chlorine). Virtually complete removal of water vapour from these gases is accomplished by a simple scrubbing operation.

Formation of Hydrolyzable Sulphates

Sulphuric acid forms hydrolyzable sulphates with many organic compounds. Many alkylation operations of the petroleum and petro-chemical industries depend on the ability of this acid to react with hydrocarbons to form intermediate compounds. Aromatic alkylamines important to the dye, photographic and pharmaceutical industries are manufactured with sulphuric acid. The production of industrially important synthetic alcohols is also based on this sulphuric acid property. (Figure 30)

Catalytic Activity

Sulphuric acid has a special catalytic properties, probably related to its affinity for water. These catalytic properties account for its large volume use in the manufacture of aviation gasoline.

Sulphonation and Sulphation

Oleum is used in the manufacture of organic sulphates. These materials, used in large quantities, are major ingredients of house-hold detergents. (Figure 29). Smaller quantities of special sulphonates are used as lubricants and as additives to automotive lubricants.

Acidulation and Neutralization

Sulphuric acid is widely used in acidulation and neutralization processes because it is frequently the most economical acid available for the job. The wide-spread use of sulphuric acid for pH control, which can also be achieved satisfactorily by any acid, is a direct result of sulphuric acid's relatively low cost and its availability. The manufacture of phosphate fertilizers is the largest singe use of sulphuric acid. Large amount of Sulphuric acid are used in acid coagulation processes (eg: GRS synthetic rubber) (Figure 26,27), and in regeneration of cationic exchange equipment.

Another major use is that of neutralization agent in production of synthetic fibers.

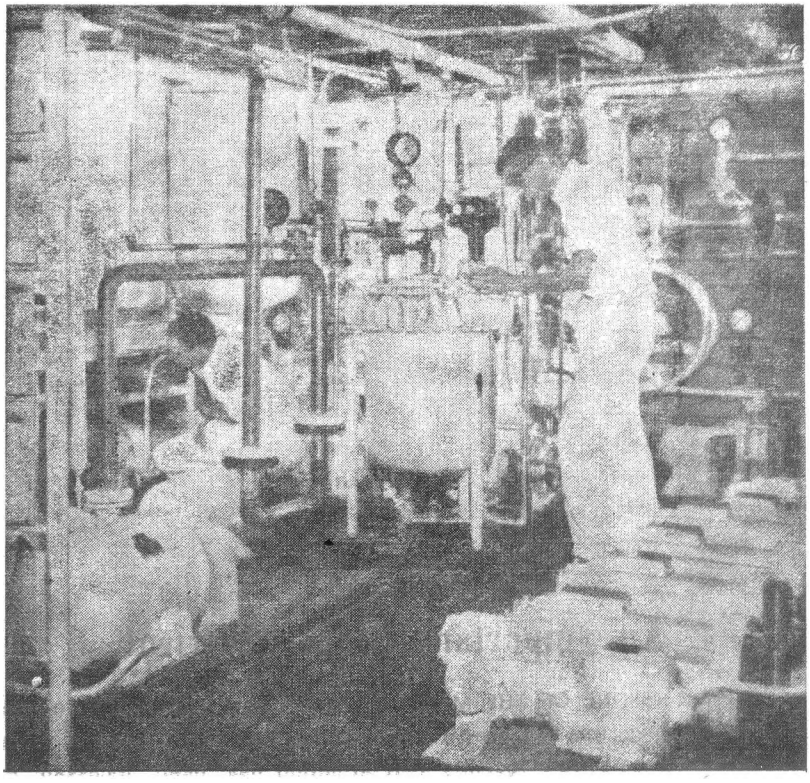


Figure 29 : Sulphonation and Sulphation– Oleum reacts with alkylbenzene and fatty alcohol to form ingredients of household detergents.
(Courtesy : Procter & Gamble Company)

Sulphur
An Important Plant Nutrient

SULPHUR IS ONE OF THE MANY elements plants require for normal growth Although this has been recognized for well over a hundred years, it is only comparatively recently that attention has been focussed on this essential plant nutrient. The immediate cause has been the appearance of sulphur deficiency on crops in an increasing number of countries all over the world. To alleviate sulphur deficiency and maintain optimum crop yields, it is necessary to ensure that sufficient amounts of sulphur are made available to the plants, and the normal way of doing this is to use fertilizer materials containing an adequate percentage of sulphur.

Why Plants Need Sulphur ?

Without sulphur, the plant can not produce protein. The amino acids methionine and cystine, which are essential in protein formation, contain sulphur. Also, a number of enzymes and vitamins contain sulphur; and onions, garlic and cruciferous plants are rich in sulphur-containing glucosides, which are often chiefly responsible for their flavour Disu'phide links have been shown to be associated with the structural characteristics of protoplasm. In some plants, the concentration of sulphydryl groups (-SH) has been shown to be related to frost resistance.

Sulphur clearly plays an essential part in plant metabolism and the amounts required by plants are quite large. Table below shows the sulphur content of several crops, compared to the nitrogen, phosphorus and potassium content.

Sulphur and Primary Nutrients Contained in Various Crops (Pounds)

CROP	YIELD/ACRE		SULPHUR[1]	NITROGEN[2]	PHOSPHORUS[3]	POTASSIUM[4]
Corn	250	Bu.	45–55	500	65	275
Cotton	3.5	Bales.	28–35	250	50	150
Wheat	80	Bu.	18–24	170	30	100
Alfalfa	10	Tons	50 60	500	50	400
Clovers	5	Tons.	25–30	250	22	165
Grasses	6	Tons.	20–35	180	27	150
Cabbage	25	Tons.	30–60	140	20	125
Turnips	30	Tons.	40–55	130	25	190
Onions	25	Tons.	30–40	130	25	90

[1] Expressed as % S (elemental)
[2] Expressed as % N (elemental)
[3] Expressed as % P (elemental), and not P_2O_5
[4] Expressed as % K (elemental), and not K_2O

Some crops (cabbage, turnips, onions) have much higher sulphur requirements than others (corn, grass). Legumes like clover and alfalfa have intermediate sulphur requirements. It is also of interest that the sulphur

and phosphorus content of many crops are of the same order of magnitude.

Crop requirements for sulphur increase as yield per hectare increases. The amount of sulphur needed is, therefore, closely related to the amount of nitrogen and other fertilizers used on the crop.

Sources of Sulphur

A review of 'how plants obtain their sulphure requirements' will also answer the question : Why sulphur deficiencies of becoming more frequent'. The main sulphur sources available to the plant are the *soil, atmospheric precipitation* and *fertilizers.*

Soil Sulphur

In soils of humid regions, most of the sulphur is contained in the soil organic matter. Soluble sulphates seldom accumulate, since they are lost by leaching. Sandy soils, low in organic matter, contain little sulphur, and it is on such soils that crops most often show sulphur deficiency symptoms. Sulphur deficiences are less frequent on soils with high organic matter content, However, fertilization with high rates of other nutrients, particularly nitrogen, may result in sulphur deficiency. Also, adverse weather conditions may retard the mineralization of soil organic matter, and hence the supply of plant-available sulphate may be insufficient at crucial growth stages.

Atmospheric Sulphur

Atmospheric precipitation contains varying amounts of sulphur, mostly originating from the combustion of fuels. Coal and certain fuel oils have a particularly high sulphur content. On burning, the sulphur content of fuels is released into the atmosphere as sulphur dioxide, and may be deposited in the soil by rainfall or absorbed directly by soils and plants. Increasing concern over pollution and quality of the environment has resulted in a gradual substitution of fuels with a low sulphur content for high sulphur coal and oil. Large tonnages of high sulphur fuel are still being used, however, but mostly in industrial areas. Inagricultural lands adjacent to such industrial areas, sulphur deficiencies are, therefore, generally absent. As air pollution regulations become more and more severe and widespread, the total amount of

sulphur dioxide emitted to the atmosphere can be expected to decrease and this source of plant nutrient sulphur is, therefore, on the decline.

Fertilizer Sulphur

Large amount of sulphur have been applied to the soil as an often unrecognized component of fertilizers. Until quite recently, two of the most widely used fertilizer materials were ammonium sulphate, containing 20% nitrogen (N) and 24% sulphur (S). and single super-phosphate containing 18% P_2O_5 and 12% S. These two materials can, with justification, be regarded equally as much as *sulphur fertilizers* than as nitrogen or phosphorus fertilizers. When sufficient amounts of these fertilizers were applied to supply the nitrogen or phosphorus requirements of the crops, the sulphur requirements were also satisfied.

Although large quantities of ammonium sulphate and single superphosphate are still being used, both materials are gradually being replaced by fertilizers with higher contents of nitrogen or phosphate, and containing little or no sulphur. Typical examples are the concentrated superphosphates containing 30-50% P_2O_5 and less than 2% sulphur, ammonium phosphates containing 11-21% N, 46-61% P_2O_5 and less than 3% sulphur, and nitrogen fertilizers like ammonium nitrate and urea which contain no sulphur at all.

Sulphur Deficiencies

Severely sulphur deficient plants may show characteristic symptoms, as they do when deficient in other plant nutrient. However, the symptoms of sulphur deficiency are not always readily distinguishable. In particular, they are frequently confused with the symptoms of nitrogen deficiency. This is hardly surprising, since both nitrogen and sulphur deficiences result in a slowlown or inhibition of protein synthesis. Some frequently encountared sulphur deficiency symptoms are listed below :

> Plants are small and spindly with short slender stalks; Growth rate is retarded and maturity is often, delayed, particularly with cereal grains, on most plants, young leaves are li ht green to yellowish in colour, with even lighter-coloured veins. On others, however, such as tobacco, citrus and cotton, some of the older-leaves may be affected first. This yellowing of the leaves is frequently confused with nitrogen deficiency symptoms. On sorghum and corn, early symptoms may also be confused with those of iron and zinc deficiencies ; On

legumes, nodulation is frequently reduced; and Fruits often do not fully mature, and are light green in colour. Spotting of leaves may occure, as with potatoes.

Less severe cases of sulphur deficiency may go unrecognized unless field trials are made to check crop yield response to sulphur applications. Soil tests for sulphur do not always provide an accurate indication of the plant-available supply of this element, and therefore can not always be relied upon for making sulphur fertilization recommendations. Analysis of plant tissue can often be of great value in determining the existence of sulphur deficiency.

Sulphur deficiencies are understood to have occur worldwide. Sulphur deficiencies have been identified in 21 of the 50 states in the USA, in 4 Canadian provinces, in 10 countries in Western Europe, in Latin America, Australia, and New Zealand, and in Africa. Several instances of sulphur deficiency and crop response to sulphur in India have been reported, and some research projects have been carried out on sulphur status on Indian soils. Sulphur deficiency has also occurred on tea, peanuts and berseem in the Punjab.

Effect of sulphur deficiency on various crops, such as: tea, paddy, jute etc has been studied and remedial actions have been proposed. Accordingly, a handsome increase of 64.5% tea yield has been achieved by using ammonium sulphate. Ammonium sulphate also increased the rice yield by 91.7%.

New Sulphur Fertilizers

The two traditional sulphur-containing fertilizers, single superphosphate and ammonium sulphate, are declining in relative importance. This tendency has been more pronounced in regions like North America and Western Europe than in India. However, the fertilizer consumption has increased rapidly in last few years.

Considerable development work has been carried out, particularly in North America, on incorporating plant nutrient sulphur in the modern, high analysis fertilizer materials. It has been observed that while the consumption of N, P and K is increasing rapidly, the amount of sulphur contained in the fertilizers is increasing at a much slower rate. To avoid lowering the NPK analysis of the materials more than absolutely

necessary, it is desirable to add sulphur in the most concentrated form possible. For this point of view *elemental sulphur* is clearly the most favoured material. Since elemental sulphur must be oxidized to sulphate before it can be utilized by plants, it is important to ensure that this oxidation takes place as rapidly as possible in the soil. Although soil conditions such as humidity, temperature, etc. are important factors affecting the oxidation of sulphur, they are generally beyond the control of the fertilizer manufacturer. However, the particle size of the sulphur is of major importance, and this is one factor which can be controlled. The smaller the particles of elemental sulphur, the more rapidly are they oxidized to sulphate. Since finely divided sulphur (80 mesh) is a difficult material to handle, much work has gone into developing a granular product which will disintegrate readily in the soil.

Granular triple superphosphate–elemental sulphur (0-40-0-20 S) has been developed by the Tennessee Valley Authority and tried out in several locations in the USA and abroad. It has proved to be a very satisfactory source of both phosphorus and sulphur and at least one fertilizer manufacturer has started production of this material. Other granular materials developed by TVA include ammonium phosphate–sulphur and ammonium polyphosphate–sulphur the latter material analyzes 12 – 51 – 0 – 15 S. These materials are presently being evaluated. Urea–sulphur (40 – 0 – 0 – 10 S) has been marketed commercially in the Western United States

A granular material containing 88% S has been developed for use in bulk blending or direct application. This material consists essentially of elemental sulphur and bentonite. In the soil, the bentonite absorbs water, swells, and thereby disintegrates the granules, resulting in finely divided and readily oxidisable sulphur.

Sulphur is soluble in anhydrous ammonia, and test programmes with a TVA material have been carried out in several regions. Field trials have shown this material, usually containing 10–12% S, to be a very effective from of both N and S, but corrosion and application, problems have delayed commercial acceptance.

Fluid fertilizers are becoming increasingly popular in the USA. Sulphur is being added to these materials often in the form of ammonium thiosulphate (12 – 0 – 0 – 20 S) or ammonium polysulphide (21 – 0 – 0 – 40 S).

Sulphur Fertilization – The Future

Most Indian soils have a low sulphur content, and the atmospheric sulphur content is also generally low. Fertilizers are thus the most important source of plant nutrient sulphur. The great advances which have recently been made by Indian agriculture, and the even greater advances expected in the coming years, will make it necessary to supply increasing amounts of sulphur to the soil. As ammonium sulphate and single superphosphate are gradually replaced by higher analysis materials, sulphur containing fertilizers suitable for Indian agricultural conditions and climates will have to be developed.

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